

CHARACTERIZATION
OF SOME
TECHNICALLY IMPORTANT
DEFECTS IN
SEMICONDUCTORS

ERIK MEIJER

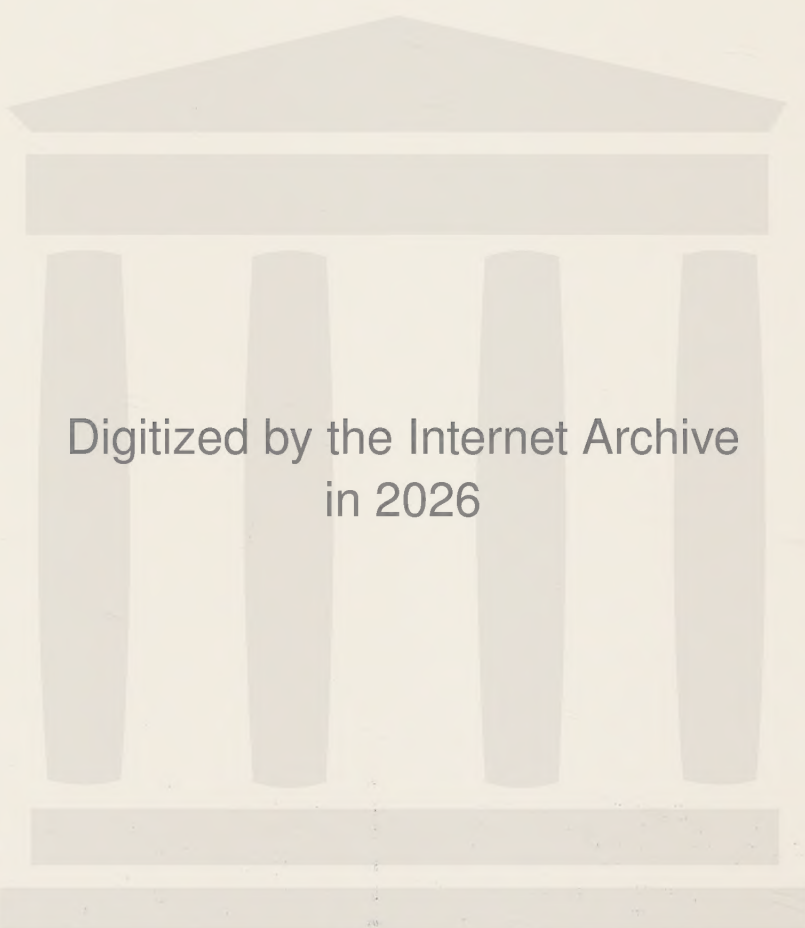


DEPARTMENT
OF
SOLID STATE PHYSICS



UNIVERSITY OF LUND
SWEDEN

1982.



Digitized by the Internet Archive
in 2026

CHARACTERIZATION
OF SOME
TECHNICALLY IMPORTANT
DEFECTS IN
SEMICONDUCTORS

ERIK MEIJER

civ ing, Ld

AKADEMISK AVHANDLING
SOM FÖR AVLÄGGANDE AV TEKNISK DOKTORSEXAMEN
VID TEKNISKA FAKULTETEN VID UNIVERSITETET I LUND
KOMMER ATT OFFENTLIGEN FÖRSVARAS I FYSISKA
INSTITUTIONENS FÖRELÄSNINGSSAL B
MÅNDAGEN DEN 29 NOV 1982 KL 10.15

Organization LUND UNIVERSITY Department of Solid State Physics University of Lund, Box 725, S-220 07 LUND, Sweden	Document name DOCTORAL DISSERTATION Date of issue 29-11-1982 CODEN: LUTFD2/(TFFF-0017)/1-144 (1982)	
Author(s) Erik Meijer	Sponsoring organization	
Title and subtitle Characterization of some technically important defects in semiconductors		
Abstract Detailed characterization of the following semiconductor/deep level impurity systems have been carried out: Gold in silicon (Si:Au), the EL2 trap in galliumarsenide (GaAs:EL2) and self-activated centers in zincsulphideselenide alloys ($\text{ZnS}_x\text{Se}_{1-x}$). The nature of these centers are still not fully understood. Mixed crystals attract additional interest as disorder systems. Space charge spectroscopy has been used. Free-carrier tail effects in pn-junctions and Schottky barriers are thoroughly described and their influence on measurements discussed. Both current and capacitance measurements are affected. Excellent agreement between theory and experiments was found. A method for elimination of displacement currents in current transient techniques is presented, leading to a considerably increased range of use of current measurements. The characteristic parameters of the gold-acceptor in Si were found to depend on the sample fabrication. The results indicate that this defect probably is a complex, and that it may involve shallow donors and oxygen. Photoionization cross sections (both for electrons and holes) of the SA-center in $\text{ZnS}_x\text{Se}_{1-x}$ is presented for the entire composition range. If the four-center model (i.e. the existence of four SA-centers differing only in the nearest anion configuration) is appropriate, then those levels seem to follow the edge of conduction band as the composition is varied.		
Key words		
Classification system and/or index terms (if any)		
Supplementary bibliographical information		Language English
ISSN and key title		ISBN
Recipient's notes	Number of pages 144	Price
	Security classification	

Distribution by (name and address)

Department of Solid State Physics, University of Lund, Box 725, S-220 07 LUND, Sweden

I, the undersigned, being the copyright owner of the abstract of the above-mentioned dissertation, hereby grant to all reference sources permission to publish and disseminate the abstract of the above-mentioned dissertation.

Signature Erik Meijer

Date 6-9-1982

CHARACTERIZATION
OF SOME
TECHNICALLY IMPORTANT
DEFECTS IN
SEMICONDUCTORS

ERIK MEIJER

LUND 1982



CHARACTERIZATION OF SOME TECHNICALLY IMPORTANT DEFECTS IN SEMICONDUCTORS

Erik Meijer

Department of Solid State Physics, University of Lund
Box 725, S-220 07 Lund, Sweden

The excitement of research in the field of solid state physics today is the potential possibilities for technical applications. Solid state devices in general, and semiconductor components in particular, are taking over an increasing number of functions in electronic systems, and the development of material and devices introduces new possibilities. The importance of the invention of the transistor is well known. The technological success of manufacturing integrated circuits also has obvious implications. Higher reliability and accuracy as well as miniaturization and reduced prices of electronic consumer goods have resulted.

The break-through of optoelectronics has already happened, even if this branch is still in its initial stage. It includes devices that convert electrical signals to optical, and vice versa. Light emitting diodes, photoconductors and phototransistors have been in use in a long time. Optical communication is expected to become increasingly important, and a substantial amount of work is being put into the design of lasers, photodetectors and optical fibers to optimize such systems. Other important optoelectronic devices are the displays, where it is desirable to obtain material that covers the whole visible spectral range.

It is expected that in the future some of the present integrated circuits in silicon will be replaced by circuits made of gallium arsenide. Electric signals travel faster in gallium arsenide and therefore this material is

more suitable for high-speed electronics. The possibility of achieving integrated optoelectronics is also apparent, since gallium arsenide has good luminescent properties.

The success of semiconductors is based on the knowledge of material technology. It is necessary to control the occurrence of impurities and imperfections to a very high degree. Absolutely pure semiconducting material is of little technical use, but by adding impurity atoms or inducing imperfections in small concentrations and in a controlled manner the properties of the host material can be drastically altered. Some impurities introduce shallow energy states into the band gap of the semiconductor. These are employed to make n- and p-type materials and to obtain junctions between n- and p-type regions. The pn junction is probably the most important concept of semiconductor technology, since it provides the basis for almost all devices. Other, less soluble, impurities give rise to deep energy states. Despite their lower concentration, the special properties they impart to the host material may nevertheless be vital. It is well known that when gold is added to silicon diodes their switching time is reduced by several orders of magnitude. Deep centers can however also be fatal to the function of a device. The presence of "killer" centers in a luminescent material is known to prevent radiative processes. The characteristic properties of a material that are governed by a deep impurity level reflect the nature of the defect. The prospect of predicting the impact of inducing certain defects makes it worthwhile to characterize such centers in great detail. Their occurrence are usually beyond the limit of chemical detection but they can be investigated by extremely sensitive electrical and optical methods.

The subject of this thesis is a detailed characterization of some defects known to be of technical importance. The concept of characterization using junction techniques is thoroughly discussed.

The work is presented in the following six papers:

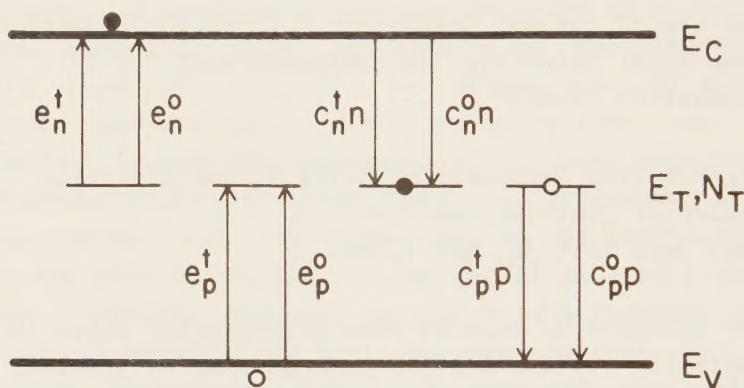
- I Complex nature of gold-related deep levels in silicon
Phys Rev B 22, 3917 (1980)
- II The use of current transients for characterization of
deep level impurities in semiconductors
Manuscript (1982)
- III Capture from free-carrier tails in the depletion
region of junction barriers
Appl Phys Lett 36, 307 (1980)
- IV The dynamics of capture from free-carrier tails in
depletion regions and its consequences on junction
experiments
Manuscript (1982)
- V Influence from free-carrier tail capture in deep level
transient spectroscopy (DLTS)
Manuscript (1982)
- VI Deep energy levels in $\text{ZnS}_x\text{Se}_{1-x}$ alloys
Manuscript (1982)

Coauthors are H G Grimmeiss (I, III-IV, VI), D V Lang and M Jaros (I), L-Å Ledebø (III-V), Zhan-Guo Wang (V) and R Mach (VI).

CHARACTERISTIC PARAMETERS

The task of characterizing a certain defect can be said to consist of two parts. First, one has to arrange and evaluate experiments that tell about the characteristic parameters. Then comes the question of physical interpretation of the experimental data. The relevant physical properties are demonstrated in the energy scheme below. The energy positions of the conduction band minimum and

the valence band maximum are E_C and E_V respectively. E_T is the energy position of the deep trap and N_T is the trap concentration. The number of deep centers is usually very small compared to the number of host atoms (less than 1 per 10 million host atoms).



Carrier transitions

The processes to be investigated are emission and capture of carriers, i.e. electrons and holes. The free carrier concentrations of electrons and holes are n and p respectively. Emission rates and capture coefficients are denoted by e and c with subscripts referring to the relevant carrier type. The superscripts indicate whether the transitions are thermal, t , or optical, o . For example, e_n^o is the rate for electron emission by absorbing photons, and $c_p^o \cdot p$ is the rate of hole capture for which energy is released as photons (luminescence). Thermal capture is nonradiative and thermal emission is governed by the absorption of thermal energy (phonons).

The absolute values, as well as the thermal and spectral dependence, of all these parameters are associated with the quantum mechanical description of the defect. From a more technical point of view those properties are decisive for whether a certain defect can be exploited for a desired device function, or whether its presence is destructive.

The benefit of doping silicon with gold has already been mentioned. The presence of gold reduces the reaction time by acting as a fast recombination center. Thus, the corresponding defect is characterized by large capture cross sections. The gold level is positioned close to the middle of the band gap and therefore acts as a rather good generator of thermal leakage current. It follows that gold must carefully be avoided in diodes designed for circuits where noise and reverse current have to be kept low.

In a photoconductor, light is detected by the induced change in conductivity. High sensitivity is achieved by using centers with large optical emission rates and small capture cross sections. In a photodiode the capture can be disregarded because of the absence of free carriers. The spectral response is determined by the trap depth.

The pn junctions are very suitable for luminescent devices because of the efficient carrier injection. Light emitting diodes exploiting deep centers emit light of a color that is determined by the energy position of the deep trap. In this case large optical capture cross sections are needed, while nonradiative capture must be negligible. Typical examples are diodes of gallium phosphide containing nitrogen (green-yellow) or complexes of zinc and oxygen (red).

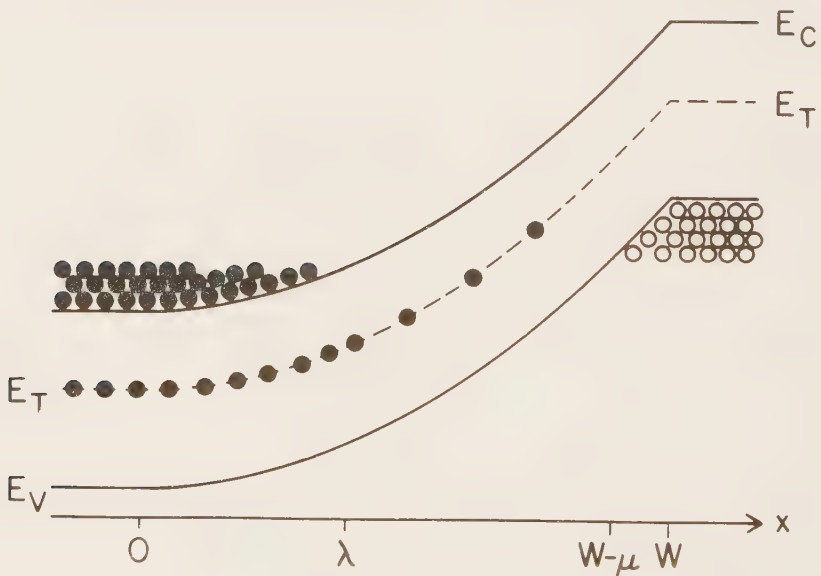
However, it is important to point out that the dopant is not the only essential factor. Rather it is the combination of host material and impurity that determines the properties of defects and devices.

DIODE PHYSICS

Many defect systems have been successfully exploited in commercial device production before their physical nature was really understood. Empirical knowledge (read trial and error) has led to device development. Defect characteri-

zation aims to a better understanding about the origin of the nature of the defect.

Suitable probe devices for deep level characterization are junction barriers, i.e. pn junctions and Schottky diodes (the latter being formed by metal-semiconductor contacts). In addition, junction barriers are interesting since they constitute the basic elements of almost all semiconductor devices. The energy diagram of a p^+n junction (heavily doped on the p-side and low doped on the n-side) is shown below. Free carriers are electrons on the n-side and holes on the p-side. Flat bands correspond to neutral material while the part where the bands are bent constitutes the space charge region. The width of the space charge region is denoted by W . A deep trap is indicated near midgap.



p^+n junction

Tails of free carriers extend into the space charge regions from the neutral material, allowing capture to occur in the edge regions (of widths λ and μ) of the space charge region. In the transition region, which is situated between the two edge regions, emission processes dominate. This is the active region used for determination of

emission parameters.

The experiments are based on altering the charge state of the centers in the transition region. This can be detected in two ways: One can measure either the current in an external circuit due to the released charge, or the capacitance change due to the change of space charge. Both the time dependence and the amplitude of the recorded signal contain information about the transition probabilities involved. Thermal parameters are determined in darkness, whereas optical experiments are performed at low temperatures where thermal emission processes are frozen out.

The different conditions that exist in different parts of the space charge region complicate the evaluation of junction experiments. Edge region effects influence all junction measurements and have to be taken into account. Sometimes the edge region effects themselves can be used constructively for the characterization.

THE SYSTEMS

Three defect systems are investigated in this thesis: gold-related deep levels in silicon, the so called EL2 trap in gallium arsenide and selfactivated centers in zinc sulphide selenide alloys. The host materials in these three cases are rather different. Silicon is a covalent semiconductor which can be grown under controlled conditions, resulting in very pure crystals. Gallium arsenide is composed of atoms from group III and V of the periodic table. The binding is slightly more ionic than in silicon. The technology of growing these crystals is also well developed. Zinc sulphide and zinc selenide represent the II-VI compounds. These crystals are substantially more ionic. Good crystal quality and high purity are hard to obtain.

Even though gold in silicon is one of the systems hitherto

most investigated, its microscopic nature is not understood yet. An acceptor level is introduced near midgap and a donor level closer to the valence band. Very detailed measurements of the acceptor in crystals grown under different conditions show that this center is more complicated than previously thought. Absolute values of optical cross sections have been found to vary in different samples. Moreover, the electron capture cross section seems to be correlated to the compensation ratio, i.e. the ratio between trap concentration and the concentration of shallow levels. The results lead to the suggestion that several very similar centers exist formed by the association of gold with some other extrinsic or intrinsic defect.

Gallium arsenide is a material of the future. Together with other III-V compounds and alloys of these it constitutes potential material for optoelectronic devices and high-speed electronics. The EL2 level appears frequently in gallium arsenide crystals. It has long been attributed to oxygen, though nowadays this is often disputed. The EL2 level is interesting since it exhibits some very characteristic properties due to a metastable excited state, and this fact allows unambiguous identification. In this thesis the GaAs:EL2 system mainly serves as a probe system for the work concerning diode physics.

II-VI compounds probably have the longest history of semiconductor application. They are usually highly luminescent and are exploited as phosphors. Their large band gaps provide the necessary condition for obtaining blue luminescence. The prospect of obtaining efficient optoelectronic devices that cover the whole spectral region attract much interest. Unfortunately, the II-VI compounds cannot be made low-ohmic in both n- and p-type. This is prevented by the high degree of local charge compensation, and therefore pn junctions cannot be formed. When donors are introduced it is energetically favourable to neutralize these by forming acceptors. They are called the selfactivated centers, and are responsible for

luminescence bands in the red for ZnSe and in the blue for ZnS. By mixing ZnSe and ZnS the luminescence shift continuously from red to blue. Such mixed crystals are also interesting as disorder systems for studying the influence of the environment closest to the defect.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to professor Hermann G Grimmeiss who introduced me to the field of semiconductor physics and provided a favourable environment for this research.

I am grateful to my coauthors for stimulating discussions and fruitful collaboration.

I thank all members of the Department of Solid State Physics for friendship and encouragement.

THE USE OF CURRENT TRANSIENTS FOR CHARACTERIZATION OF DEEP LEVEL IMPURITIES IN SEMICONDUCTORS

E Meijer

Department of Solid State Physics, University of Lund
Box 725, S-220 07 Lund, Sweden

In conventional current transient measurements in diodes the excited charge from centers in the depletion region is distributed between the measurable external current and the internal displacement current. The relative magnitude of those currents are of importance for the evaluation and is described by the so called D-factor. The nature of D is discussed. Equations for theoretical derivation are given and techniques for experimental determination are described. Excellent agreement was found between theory and experiments. A technique for elimination of displacement currents is also presented, increasing the range of use of current transient methods.

NOTATION

A	Junction area
C	Junction capacitance
c_n, c_p	Capture coefficient for electrons and holes
D	D-factor
e_n, e_p	Total emission rate of electrons and holes, $e_n = e_n^o + e_n^t$
e_n^o, e_p^o	Optical emission rate of electrons and holes, $e^o = \sigma^o \Phi$
e_n^t, e_p^t	Thermal emission rate of electrons and holes
e	Electron charge
$\epsilon \epsilon_0$	Dielectric constant of the semiconductor
Φ	Photon flux
E_C, E_V	Energy position of conduction band and valence band edge
E_T	Energy position of the deep trap
F_n, F_p	Quasi Fermi levels for electrons and holes
I^o, I^t	Optical and thermal generation current
k	Boltzmann factor
λ^o, λ^t	Width of the λ -region in the optical and thermal case
μ^o, μ^t	Width of the μ -region in the optical and thermal case
N_T	Total concentration of deep traps
n_T, p_T	Concentration of traps occupied by electrons and holes
N	Concentration of shallow levels
n, p	Free carrier concentration of electrons and holes
σ_n^o, σ_p^o	Photoionization cross section for electrons and holes
T	Temperature
t	Time
τ	Time constant
V_d	Junction diffusion voltage
V_r	Applied reverse voltage
$Q_T, \Delta Q$	Charge

I. INTRODUCTION

Impurities that give rise to deep electronic energy states in the band gap of the host semiconductor are often important for the function of semiconductor devices, even though they may be present in very small concentrations. The device can either rely on the special properties governed by the incorporation of some impurity, or the presence of a certain impurity can be fatal to the desired function.

A typical example of a technically important impurity is the gold related center in silicon, known to reduce the switching time of diodes by several orders of magnitude. In this paper we will use a gold doped silicon diode as a probe system.

The most important physical properties are the thermal and optical transition rates of both electrons and holes between the impurity state and the bands. These characteristic parameters as well as concentration profile and binding energy can be determined from experiments. Junction barriers, i.e. Schottky diodes and pn junctions, have frequently been used. Then changes of the impurity charge state are observed by monitoring either current or capacitance signals. These techniques are described in comprehensive review articles.¹⁻³

A difference between the two techniques is that while the current originates only from the deep centers, the capacitance signal is superposed on the total diode capacitance. Thus, also the steady state current can be exploited in the evaluation of emission rates. Current transient methods are perhaps less popular than capacitance techniques. We believe that this is partly due to the problem of taking displacement currents in depletion regions correctly into account.

The purpose of this paper is to describe the displacement current contribution to current transients, and how

corrections can be made for a proper evaluation of concentration profiles and emission rates. The value obtained for the binding energy is also influenced since it is determined from the emission rates. We will also present a transient technique that eliminates displacement currents, which has several useful consequences.

II. THEORY

It has been shown that the generation current from deep impurities in a p^+n junction originates only from a certain volume, the transition region, within the total space charge region.⁴ The contribution from the transition region dominates over the current generated in the edge regions, i.e. the regions where the capture from free carrier tails, extending into the space charge region from neutral material, is much more efficient than the carrier emission processes.⁵ As a consequence only impurity centers within the transition region can be made to change their charge state, and this influences the displacement current.⁶

Consider the reverse biased p^+n junction shown in Fig 1a. The depletion region is entirely in the lower doped n -type material and the deep impurity is assumed to be present in a small concentration compared to the concentration of shallow donors. The system corresponds to the gold related acceptor in silicon which is negatively charged when occupied by an electron. The scale of the x -axis is defined by zero electric field at $x=0$. Thus, the interface between the p - and n -type material is at $x=W$, where W is the total width of the space charge region. The transition region is between $x=\lambda$ and $x=W-\mu$, and the widths of the two edge regions are λ and μ respectively.

Obviously λ and μ are the essential parameters and we must start to calculate these. For this purpose the relevant transitions between the deep center and the bands are shown in Fig 2. In neutral material the capture processes are dominant since the free carrier concentrations are

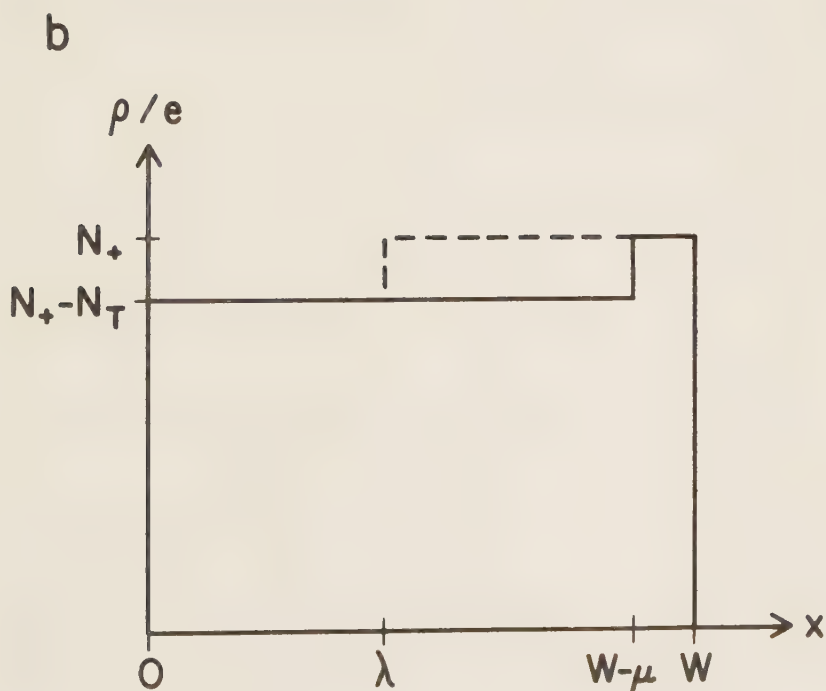
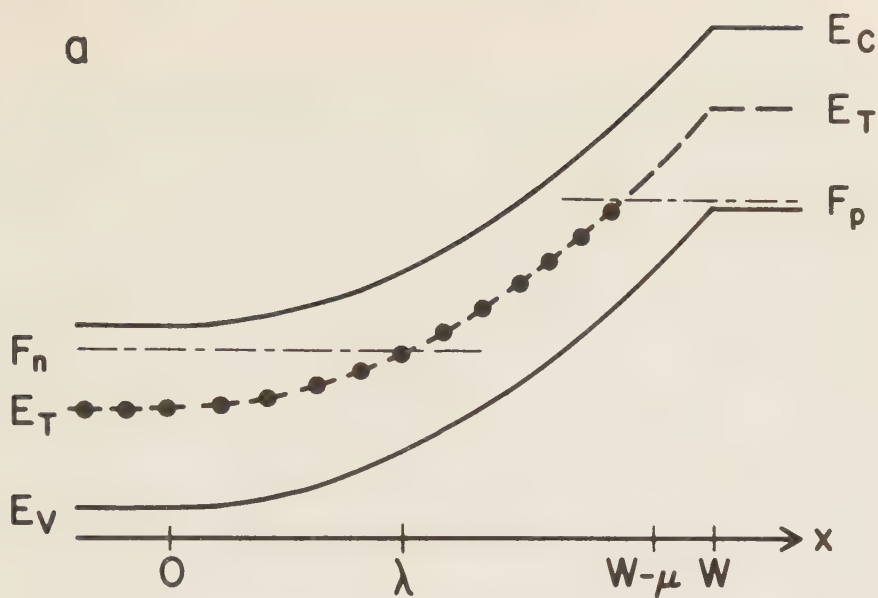


Fig 1. a) Energy band diagram for a reverse biased Si p^+n junction with the gold acceptor level. The edge region widths λ and μ are indicated on the x -axis. b) Charge density distribution for the same junction. The solid line corresponds to the situation when the centers in the transition region are occupied by electrons and the dashed line describes the change when these electrons have been removed.

large. Entering the depletion region the free carrier concentrations decrease exponentially with the energy band bending. The capture rates decrease accordingly and soon the emission processes become dominant. The volumes where emission and capture processes are of the same order are very small because of the rapid change in free carrier concentration with distance. The resulting charge density distribution of the deep acceptors can therefore be regarded as a stair-case function: In the λ -region electron capture establishes the electron occupancy to one and in the μ -region the occupancy is zero due to the hole capture while in the transition region the occupancy is determined by the ratio between electron and hole emission rates. It is the dividing-lines between these regions that we need. They can be calculated from the rate equation for the processes of Fig 2, knowing the electrostatic potential of Fig 1a, by defining the boundaries as the positions where the occupancy is the average of the occupancies in the surrounding regions.

The derivation of λ and μ is given in Appendix A. The boundary conditions are shown to result in the following requirements

$$n(\lambda) = \frac{e_p + e_n}{c_n} \quad (1)$$

$$p(W-\mu) = \frac{e_p + e_n}{c_p} \quad (2)$$

These are the same boundaries as found by Braun and Grimmeiss⁴ for the active volume for steady state generation current by studying the denominator in the expression for the total net emission rate. Thus, the transition regions for steady state and transient current are the same. The resulting equations for λ and μ can be separated into two special cases, the optical case when thermal emission rates are negligible and the thermal case when no optical excitation is present. We have for the optical case

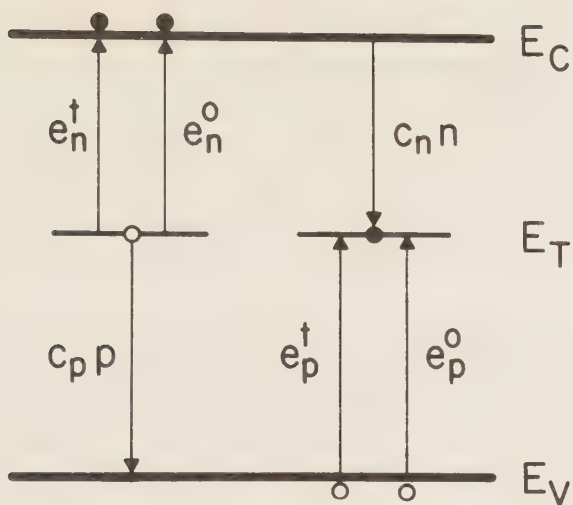


Fig 2. Energy band diagram showing the possible capture and emission processes appropriate to the Si: Au_{acc} system.

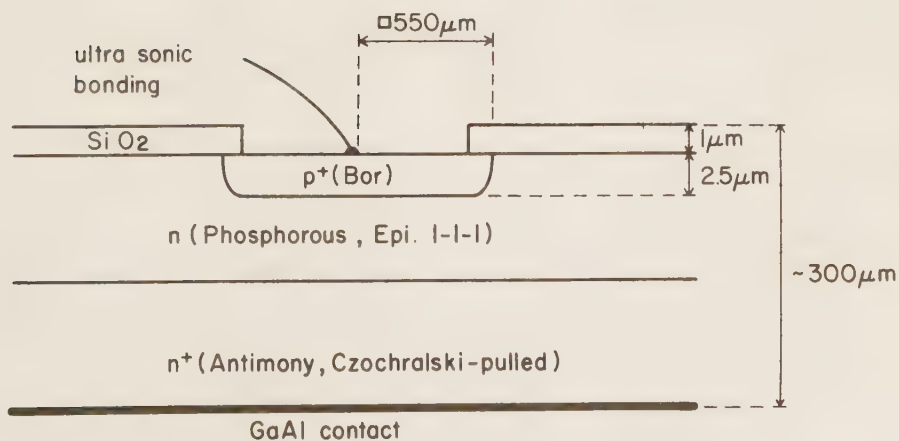


Fig 3. Schematic drawing of the gold doped silicon p⁺n junction used.

$$\lambda^0 = \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \frac{kT}{e} \ln(c_n n(0)\tau^0) \right\}^{1/2} \quad (3)$$

$$\mu^0 = W - \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \left[V_r + V_d - \frac{kT}{e} \ln(c_p p(W)\tau^0) \right] \right\}^{1/2} \quad (4)$$

where $\tau^0 = (e_p + e_n)^{-1}$ is the time constant of the optical transient induced by light capable of changing the initial occupancy. In the thermal case the time constant for thermal emission can be evaluated theoretically and we arrive at

$$\lambda^t = \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \left[\frac{(F_n - E_T)_n}{e} - \frac{kT}{e} \ln\left(1 + \frac{e_p^t}{e_n^t}\right) \right] \right\}^{1/2} \quad (5)$$

$$\mu^t = W - \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \left[V_r + V_d - \frac{(E_T - F_p)_p}{e} + \frac{kT}{e} \ln\left(1 + \frac{e_n^t}{e_p^t}\right) \right] \right\}^{1/2} \quad (6)$$

where $(F_n - E_T)_n$ and $(E_T - F_p)_p$ are the separations between the quasi Fermi levels and the trap energy level in the neutral n- and p-type material respectively.

It is clear that λ does not depend on the applied reverse bias whereas μ is weakly voltage dependent. The transition region is in the optical case determined by the balance between the capture rates and the optical time constant. In the thermal case the positions depend on a similar balance but include the thermal time constant instead. Since this time constant is the reciprocal sum of the thermal emission rates, λ^t and μ^t are more directly related to the energy position of the impurity state.

Having established the position and width of the transition region we can derive an expression for the fraction of the charge excited in this region that builds up the displacement current. Returning to the diode in Fig 1a we consider an initial state where all deep centers are

occupied by electrons except those in the μ -region which are always empty. The corresponding charge density distribution is described by the solid line in Fig 1b, Now we excite all trapped electrons within the transition region to the conduction band, keeping the applied reverse bias constant. The total released charge is

$$Q_T = eA (W - \lambda - \mu) N_T \quad (7)$$

The change in the charge density distribution, described by the dashed line in Fig 1b, induces a small shift of the depletion layer width to $W - \Delta W$. For this purpose some of the excited charge, ΔQ , is needed for compensation of space charge:

$$\Delta Q = eA(N - N_T) \Delta W + eAN_T \Delta(W - g) = eAN \Delta W \quad (8)$$

ΔQ builds up the displacement current and the rest of the excited charge, $Q_T - \Delta Q$, is free to pass through the outer circuit and add to the negative space charge on the p-side of the junction. This charge builds up the measured current transient. The factor D is defined by the ratio between the total number of excited electrons and the number of electrons detected in the transient in the external circuit,⁶ i.e. for electrons

$$D^{-1} = \frac{Q_T - \Delta Q}{Q_T} \quad (9)$$

The D-factor for hole excitation, D_p , can be determined by performing the reverse procedure. The hole charge Q_T is excited to the valence band in the transition region, and the portion ΔQ will pass through the external circuit and add to the positive space charge as the depletion layer width increases from $W - \Delta W$ to W . We get for the hole D-factor expressed in D

$$D_p^{-1} = \frac{\Delta Q}{Q_T} = 1 - D^{-1} \quad (10)$$

The change ΔW is calculated by solving the Poisson equation for the electrostatic potential for the charge

density distributions shown in Fig 1b:

$$\Delta W = \frac{N_T}{N} \frac{(W-\lambda)^2 - \mu^2}{2(W - \frac{N_T}{N}\lambda)} \quad (11)$$

Here higher order terms in ΔW have been omitted. The resulting expression for the D-factor is then

$$D^{-1} = 1 - \frac{W - \lambda + \mu}{2W(1 - \frac{N_T}{N} \frac{\lambda}{W})} \quad (12)$$

D^{-1} tells us how much of the excited charge, due to a variation of charge states of centers in the transition region, that contributes to the current transient we can measure in the external circuit. A general expression for the generation current as a function of time can now be derived by solving the rate equation (see eq (18) in Appendix A) and take D into account. The current is³

$$I(t) = eA(W-\lambda-\mu) [D^{-1}e_n n_T(t) + (1-D^{-1})p_T(t)] \quad (13)$$

and the electron occupancy in the interior of the transition region is

$$n_T(t) = n_T(\infty) + [n_T(0) - n_T(\infty)] e^{-\frac{t}{\tau}} \quad (14)$$

where the time constant $\tau = (e_p + e_n)^{-1}$ and $n_T(\infty) = e_p \tau N_T$. The hole occupancy is $p_T(t) = N_T - n_T(t)$. Naturally the displacement factor D does not affect the steady state generation current, which is

$$I(\infty) = eA (W-\lambda-\mu) N_T e_p e_n \tau \quad (15)$$

After having established a certain initial state for the occupancies a typical current transient experiment is performed by measuring the steady state current, and from the exponential part of the current transient determine the time constant and the initial current, $I(0)$, by extrapolation. Then the emission rates are calculated from the time constant and the ratio between the initial and

the steady state current:

$$\frac{I(0)}{I(\infty)} = \frac{p_T(0)}{p_T(\infty)} + D^{-1} \left[\frac{n_T(0)}{n_T(\infty)} - \frac{p_T(0)}{p_T(\infty)} \right] \quad (16)$$

It is thus clear that the factor D is of great importance for a correct determination of the emission rates.

III. EXPERIMENTAL DETAILS

When gold is incorporated into silicon an acceptor and a donor level are introduced in the band gap.⁷ The acceptor level is placed 0.55 eV below the conduction band minima from thermal⁸ and optical⁷ current measurements. The donor level is closer to the valence band,⁷ and we will operate the sample in such a way that the donor will not be affected.

The measurements were performed on a gold doped silicon p^+n junction (Fig 3). The resistivity of the epitaxial n -type substrate was 10 Ωcm . Gold diffusion was made at 825°C for one hour from a 200 nm thick layer of pure gold deposited by evaporation on the bottom surface of the substrate. Then the diode was quenched to room temperature in air.

The concentrations of both the shallow phosphorus donor and the deep gold acceptor were constant in the depletion region, and were found to be $8.5 \cdot 10^{14} \text{ cm}^{-3}$ and $1.1 \cdot 10^{14} \text{ cm}^{-3}$ respectively. The optical photoionization cross section spectra of electrons and holes are shown in Fig 4, measured by photocapacitance spectroscopy at 80 K.

An obvious way to determine D experimentally is to copy the procedure used for the theoretical derivation, and measure the charge in the current transients when only electrons and only holes are released. This is however often not possible because in general only one of the transients can be obtained without simultaneous excitation of both electrons and holes. It is possible to work out a model that takes two-step excitation into account⁶ but the

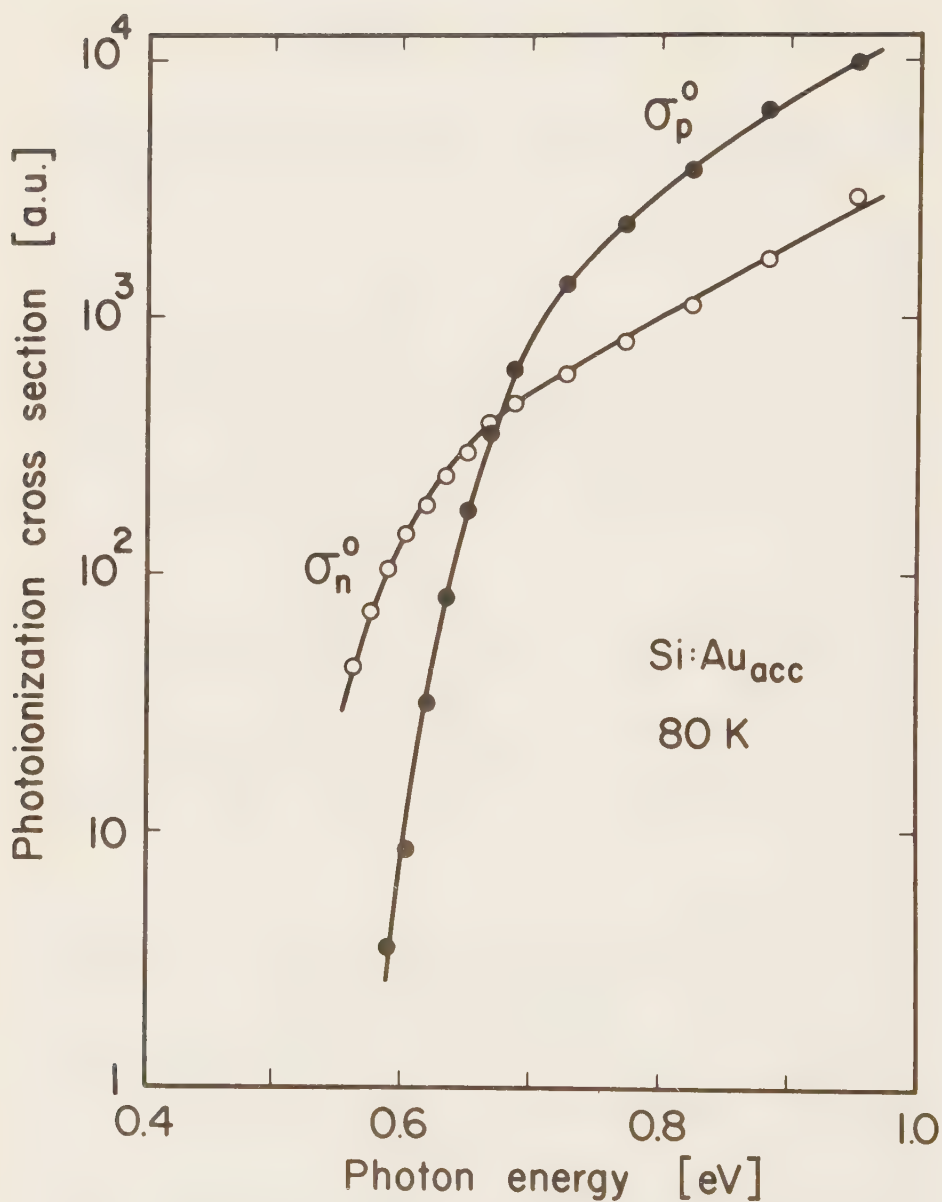


Fig 4. Photoionization cross section spectra for electrons σ_n^0 , and holes σ_p^0 , at 80 K.

resulting method becomes rather laborious.

From the dependence of the capacitance transient amplitudes on applied voltage both W and λ can be deduced.⁹ The missing parameter for the derivation of D according to eq (9) is μ (if the compensation ratio N_T/N is known). Also this method requires substantial experimental work.

We will present here another technique which is simple and does not involve any transient measurements. It can be used when two-step excitation is present and it renders all the widths W , λ and μ . In addition information about energy depth and concentration of the deep center is obtained. The steady state current and capacitance are measured as a function of voltage. The current is plotted against the corresponding depletion layer width given by $W = \epsilon \epsilon_0 A / C$. From eq (15) follows that the current grows asymptotically linear with W since μ is negligible at higher reverse voltage and λ is voltage independent. The asymptot intercepts the W -axis at λ and its slope is proportional to N_T . μ is given by the distance between the asymptot and the measured values of W at constant steady state current (as soon as $eV_r \gg kT$).

Such a plot is shown in Fig 5 for our gold doped silicon diode at room temperature. The diode was kept in dark. Thus, the generation current is only due to thermal processes. Eq (5) tells us that λ^t , given by the intercept of the asymptot with the W -axis, is directly related to the trap depth since the second term is negligible when e_p^t/e_n^t is small, which is true in our case. Taking the Fermi level into account we get $E_C - E_T = 0.54$ eV which is close to published values.⁸ From the plot of Fig 5 the D -factor is determined by reading values of W and μ^t together with the constant λ^t , at each reverse bias.

A similar plot for the optical case is shown in Fig 6. The diode was illuminated with monochromatic light ($h\nu = 0.73$ eV) at 80 K. The resulting λ^0 is $0.41 \mu\text{m}$. This is quite close

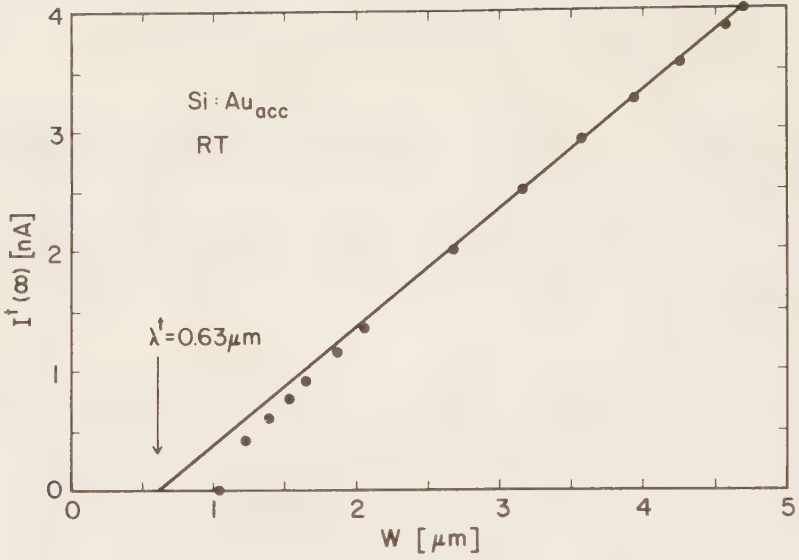


Fig 5. Thermal generation current versus depletion region width at room temperature.

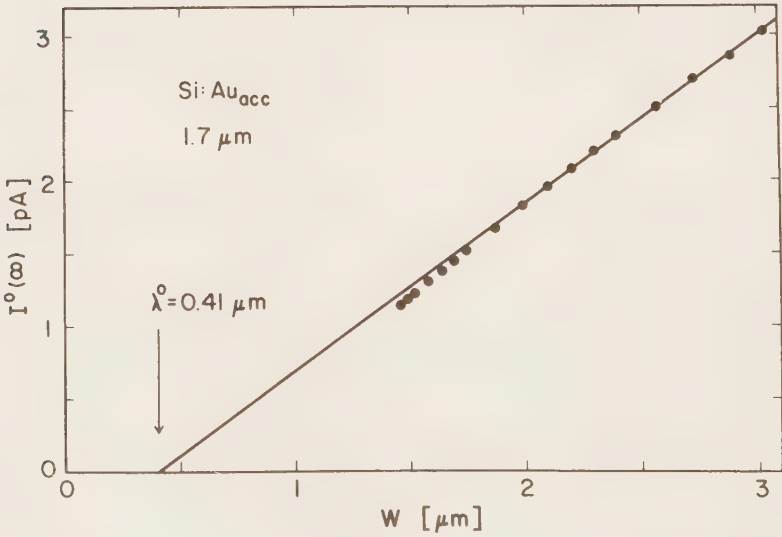


Fig 6. Optical generation current versus depletion region width for light of wavelength 1.7 μm .

to the theoretical value of $0.42 \mu\text{m}$, calculated by eq (3) using the measured optical time constant $\tau^0=2 \text{ s}$, and the capture coefficients $c_n=1.5 \cdot 10^{-9} \text{ cm}^3/\text{s}$ and $c_p=8.2 \cdot 10^{-7} \text{ cm}^3/\text{s}$.^{8,10} We note also that in the case of thermal equilibrium the theoretical width of the λ -region becomes $0.93 \mu\text{m}$, i.e. more than twice as large as λ^0 . This clearly demonstrates that at temperatures where emission processes are frozen out λ is determined by the capture cross section and are not related to the trap binding energy.^{5,11}

We will also estimate D in the optical case by fitting eq (16) to experimental data. Optical transients are measured for various photon energies. The initial occupancy is also established by illumination, and the initial and final occupancies are given by the photoionization cross sections in Fig 4. The D-factor comes out as the fitting parameter.

IV. NATURE OF THE D-FACTOR, CALCULATIONS AND EXPERIMENTS

The use of current transients for the determination of thermal activation energies, optical threshold energies and concentration profiles relies on the knowledge of the D-factor. We will show which parameters that influence D and in some cases make comparison with experiments.

It is obvious that the space charge density distribution is of importance for the value of D. The concentration profiles of both shallow and deep impurity centers affect the expressions for λ and μ via the electrostatic potential. The boundary conditions (1) and (2) are always true but the equations for λ and μ (eq (3)-(6)) are only valid for a junction with a parabolic band bending. Such a potential corresponds to a diode with constant shallow doping and deep centers in a small concentration which is also constant. Our probe diode fulfills these requirements and we will in the following discuss this case only.

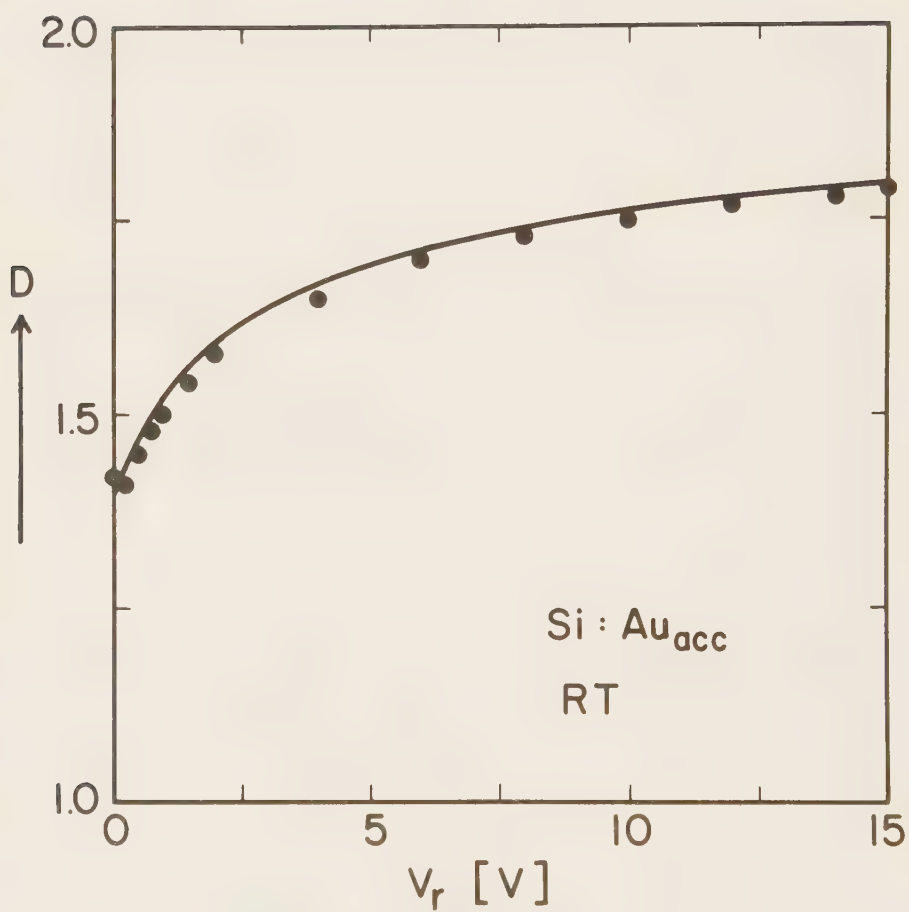


Fig 7. D as a function of reverse bias in the thermal case at room temperature. The solid line is the corresponding theoretical calculation.

D is influenced by the following parameters:

- 1 Temperature
- 2 Applied voltage
- 3 Energy depth (thermal case)
- 4 Capture cross section and time constant (optical case)
- 5 Active volume (profiling experiments)

1. The explicit temperature dependence of D can be seen in the expressions for λ and μ (eq (3)-(6)), but more indirect influences are present as well. The quasi Fermi levels vary with temperature which in turn affect the diffusion voltage, and the temperature dependent Fermi function determines the energy distribution of free carriers. The energy position of the trap can vary with temperature with respect to one or both energy band edges, and in general also the emission rate ratio and the capture cross sections depend on the temperature. Thus, the total temperature dependence of the D-factor is rather complicated, even though not very strong.

2. More straight-forward is the variation of D with the applied voltage. While λ is always constant both W and μ are voltage dependent. W is roughly proportional to the square root of V_r and μ decreases rather rapidly with increasing V_r . According to eq (12), this means that D increases with V_r starting from a value less than two and asymptotically approaches two. For the thermal case we extracted λ together with W and μ at different reverse biases from Fig 5. The D-factor was calculated and is plotted in Fig 7. Also shown is a theoretical calculation of D obtained from eq (5)-(6) and (9). The D-factor for the optical case obtained from the data in Fig 6 is shown in Fig 8 together with the corresponding theoretical curve (according to eq (3)-(4) and (9)). In both cases the agreement is good. The optical D-factor is somewhat larger than the thermal one. This is expected because of the larger transition region in the optical case.

3. The energy position of the deep state is decisive for

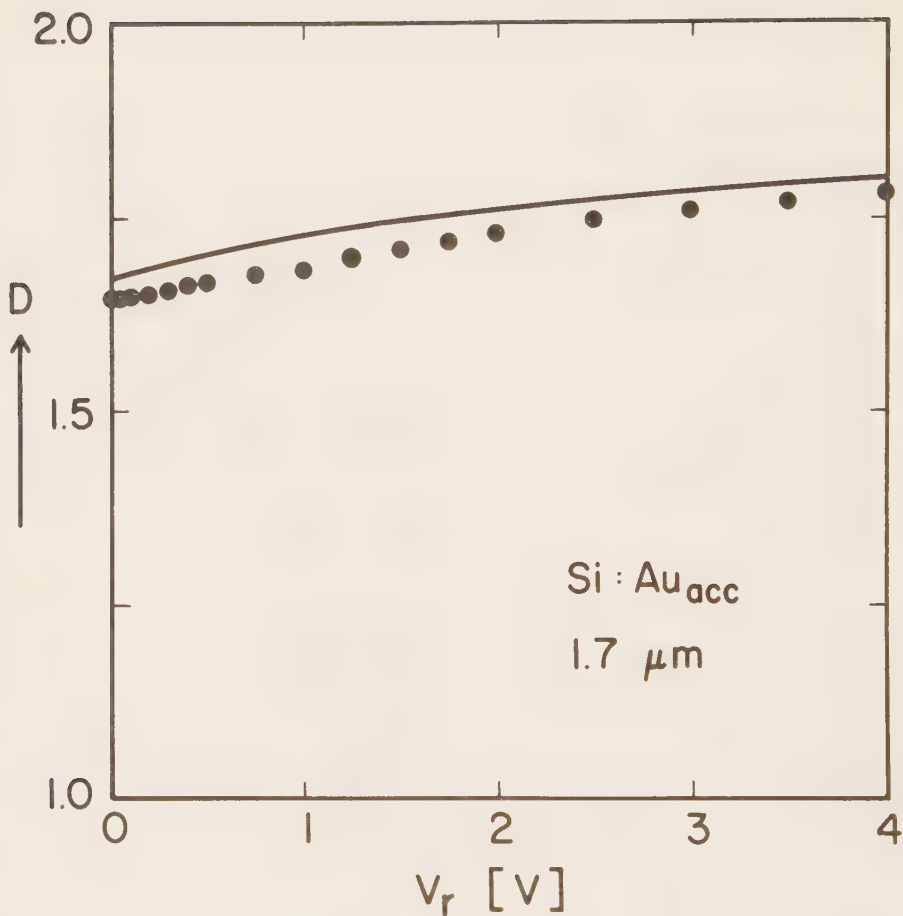


Fig 8. D as a function of reverse bias in the optical case at 80 K for light of wavelength $1.7 \mu\text{m}$. The solid line is the corresponding theoretical calculation. The optical time constant was $\tau^0=2 \text{ s}$.

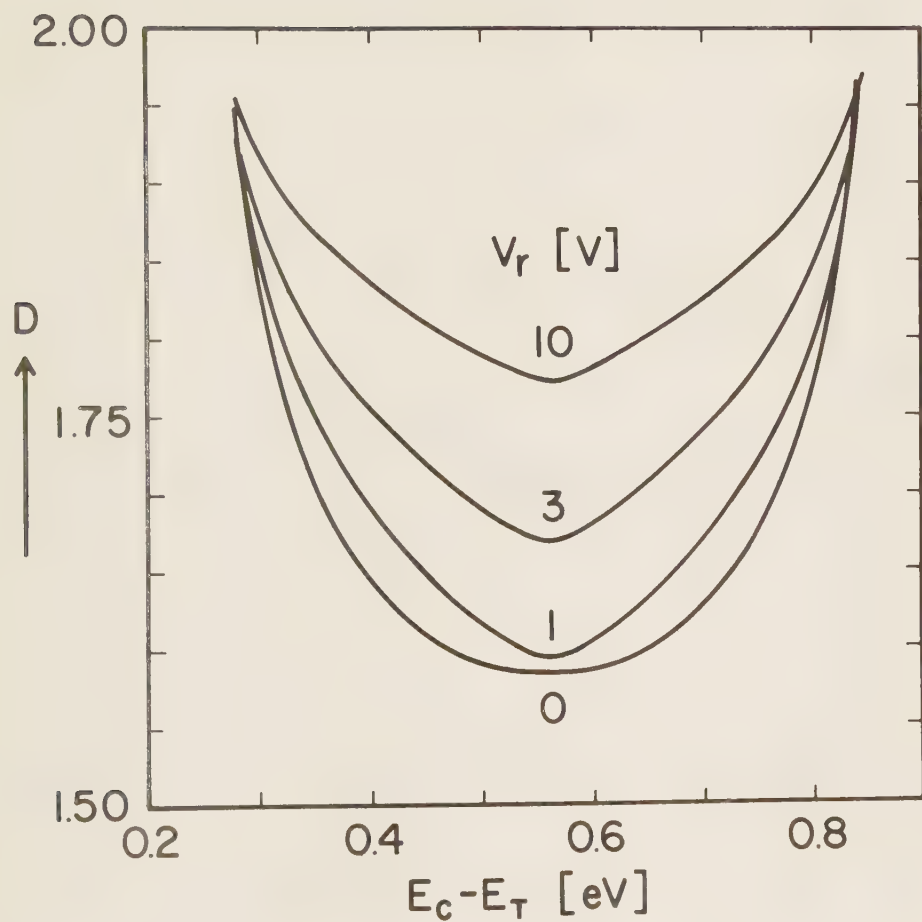


Fig 9. Theoretical calculation of D as a function of trap depth for the thermal case at 300 K in a Si p^+n junction, and for various reverse biases, using $c_n/c_p=1$, $V_d=0.7$ V and $(E_C - E_n)_n=0.27$ eV.

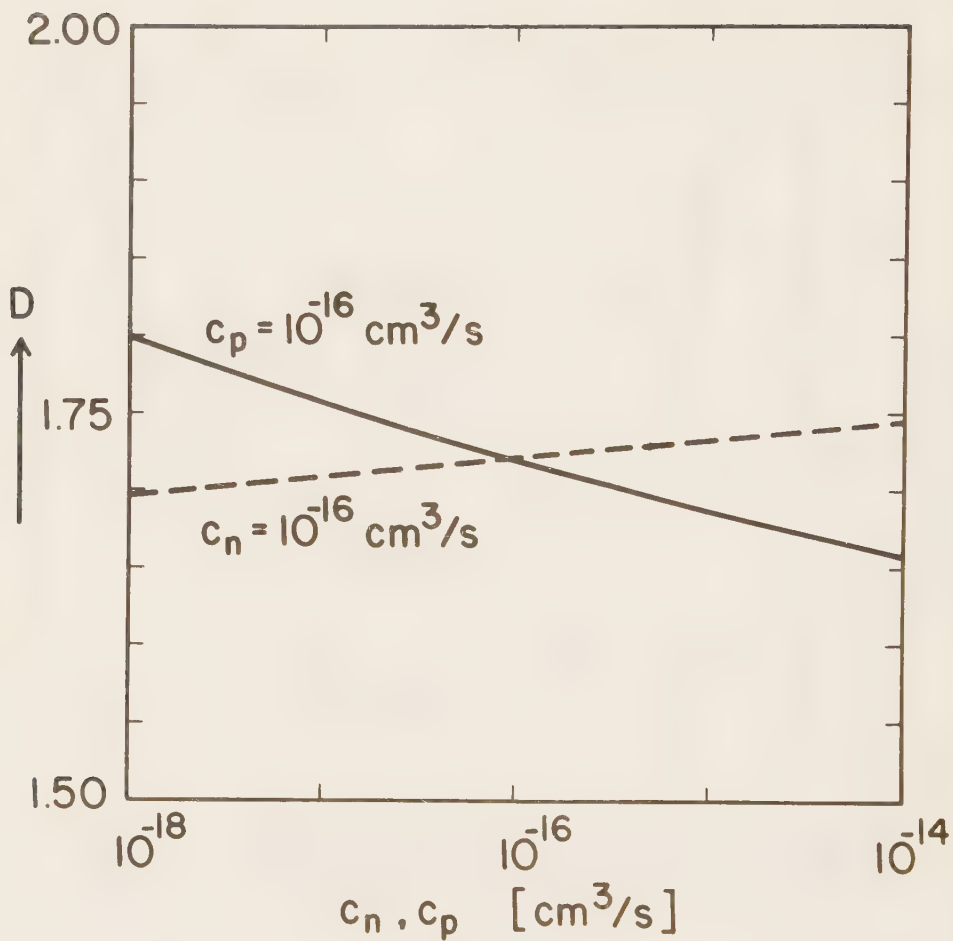


Fig 10. Theoretical calculation of D as a function of the electron and hole capture coefficients keeping one of them constant at a time. The calculation applies to a Si p^+n junction in the optical case at 80 K for the optical time constant $\tau^0=1$ s.

the D-factor in the thermal case. This is clear from eq (5)-(6) which include both the relative position to the quasi Fermi levels and the thermal emission rates that depend exponentially on the energy distance to the respective energy band. The situation is demonstrated in Fig 9 for a typical silicon pn junction at room temperature, and for a few different reverse biases. It can be concluded that D has a minimum when the energy level is close to the middle of the band gap. The deeper the trap is, the better can capture compete with emission and the smaller becomes the transition region. Thus it is understandable that the deepest centers have the smallest D-factors.

4. It is always the balance between capture and emission processes that determines D, through the edge region widths λ and μ . In the thermal case the emission rates are directly related to the activation energies, but in the optical case the capture competes with optical emission which depends on photoionization cross sections and photon flux. Given a certain time constant for the optical transient, τ^0 , the D-factor depends on the capture coefficients for electrons and holes as indicated in eq (3)-(4). Numerical calculations are shown in Fig 10 for a representative silicon p⁺n junction at 80 K. D is not very sensitive to variations in the capture coefficients due to the logarithmic dependence. As expected the D-factor varies more with the majority carrier capture coefficient than with the minority carrier capture coefficient.

5. The largest changes in the D-factor are obtained when the active volume is allowed to vary. The active region refers to the part of the junction in which the trap charge states are altered. Usually and as has been discussed so far, the active region coincides with the transition region, i.e. the region that contributes to steady state generation currents. Sometimes it is useful to keep these regions different. When concentration profiles are to be determined it is of interest to vary the active region while the transition region is constant.

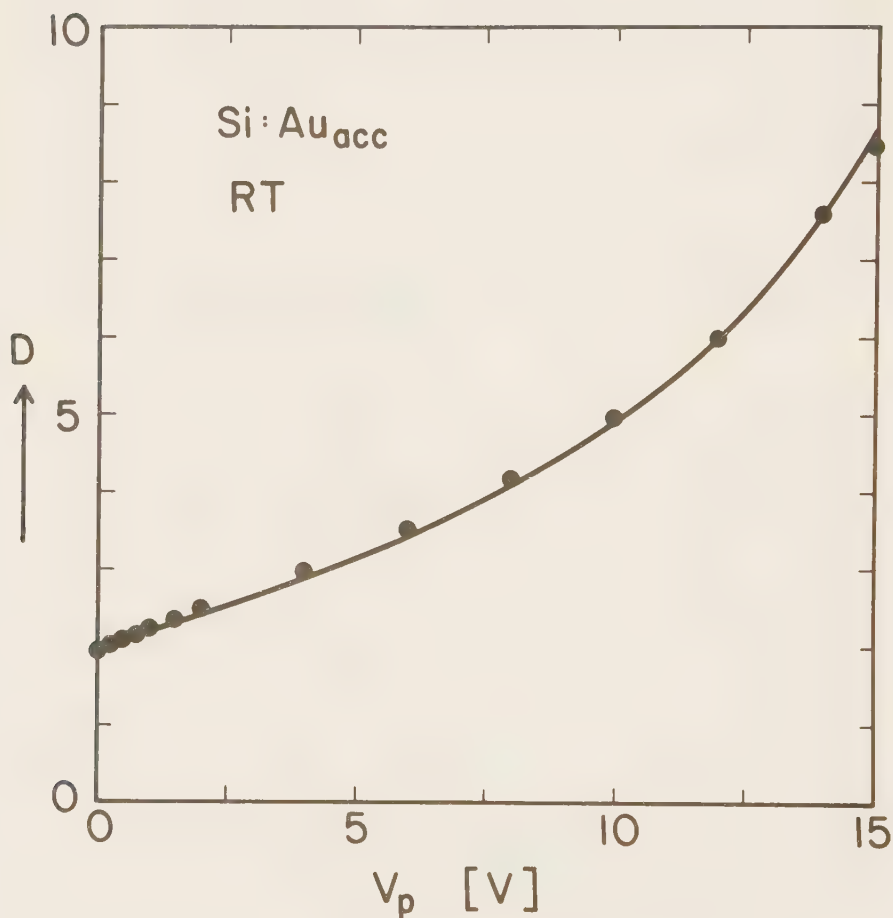


Fig 11. The influence of the active volume on D in the thermal case for the Au_{acc} in Si at room temperature. The reverse bias was $V_r=15$ V. V_p is the applied voltage used for electrical pumping of the deep centers. The line is the corresponding theoretical calculation.

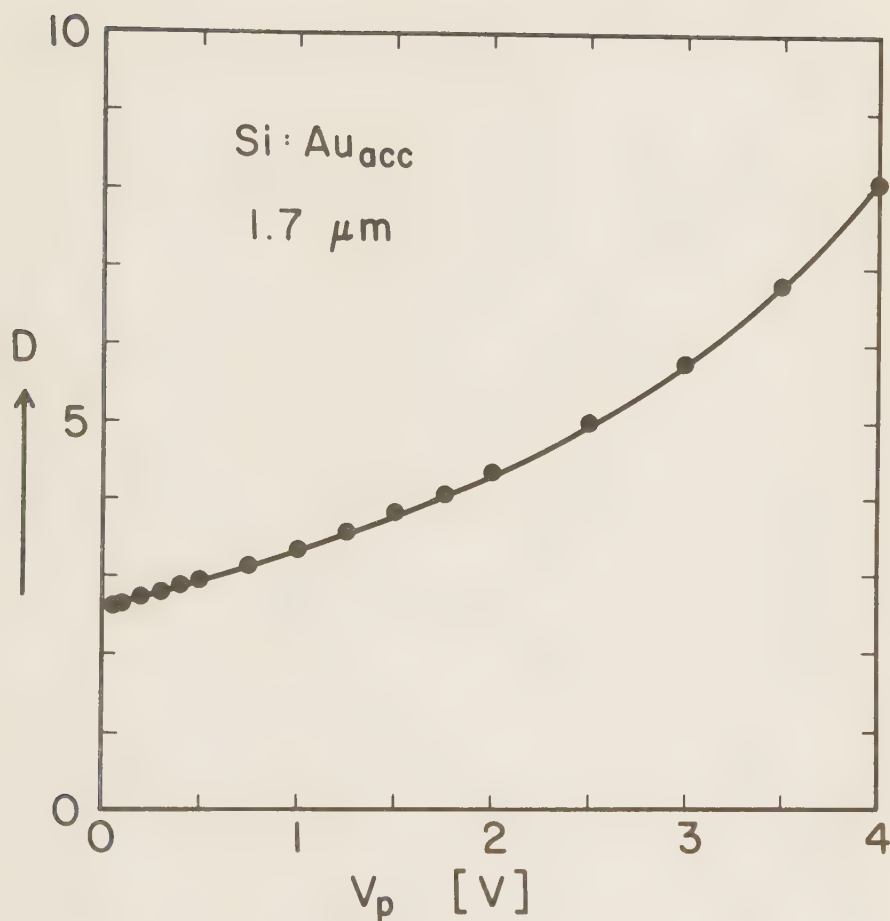


Fig 12. The influence of the active volume on D in the optical case for the Au_{acc} in Si at 80 K. The light wavelength was 1.7 μm and the optical time constant $\tau^0=2\text{s}$. The line is the corresponding theoretical calculation.

This can be realized by lowering the reverse bias from V_r to a certain value V_p which is the parameter, allowing for majority carrier capture in a volume confined between λ and $\lambda + W(V_r) - W(V_p)$. Then the bias V_r is restored. If the experiment is an optical one it is necessary to illuminate the sample during the pumping, in order to establish the occupancy in the rest of the transition region to be the same as the final occupancy in the active region. Thus, the steady state current originates from the whole transition region whereas the transient current is generated only in the active region. To derive a D-factor for such a transient, eq (12) has to be modified. One of the active region boundaries, λ , is always the same. The other is varying with the pumping voltage, V_p , and μ in eq (12) has to be exchanged by $W(V_p) - \lambda$. Also in this case we can use Fig 5 and 6 for experimental determination of D for the thermal and optical cases. The experimental results are compared with theoretical calculations in Fig 11 and 12. The agreement is good. It can be seen that the variation of D is substantial, and serious errors can be made if a correct D-factor is not taken into account in the transient evaluation.

The variation of D in a profiling experiment as described above does in fact reflect the sensitivity of capacitance and current measurements for different parts in the depletion region. A large D-factor implies a relatively small current and large capacitance change. The closer to the lower doped neutral material the active region is positioned, the larger is D. Thus, excited charge contributes relatively more to capacitance signal and less to current signal the closer to the λ -region our active volume is situated.

We will finish this section by discussing the influence of D on the current transient waveform. In optical measurements both the initial and the final occupancies can be chosen arbitrarily if the photoionization cross sections (Fig 4) are known. Then the waveform is given by eq (16). For the requirement $I(0)/I(\infty)=1$ two solutions can

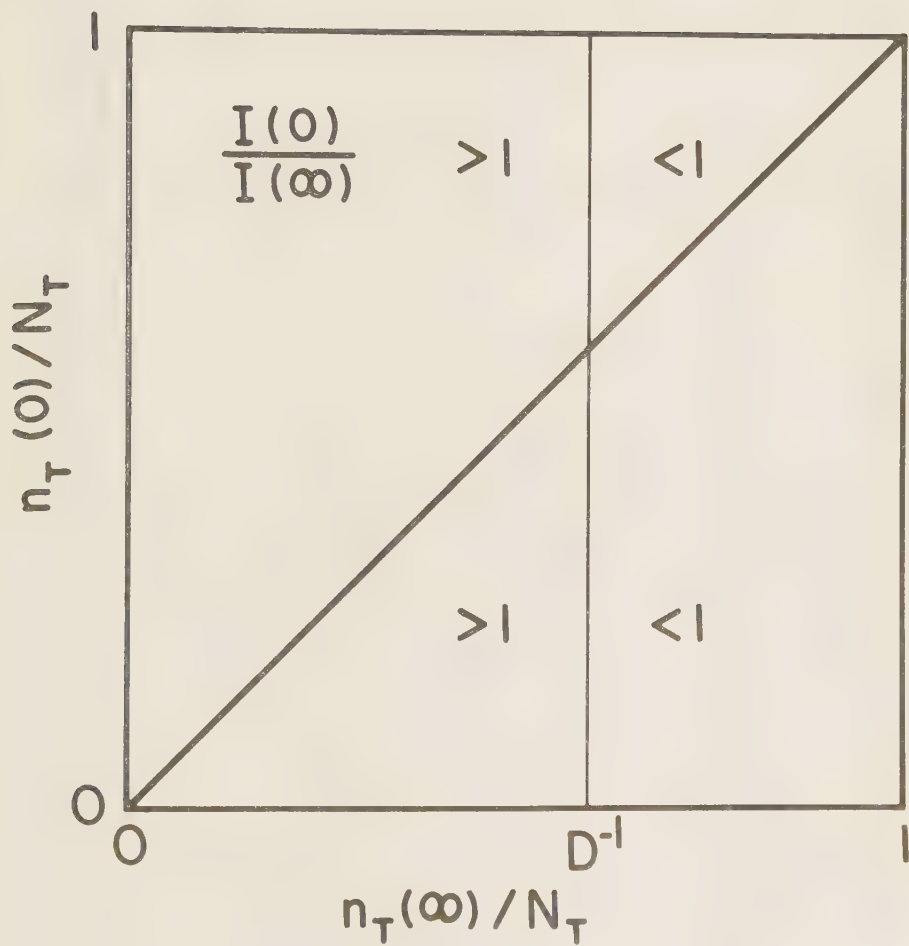


Fig 13. Current transient waveform scheme as a function of initial and final electron occupancies.

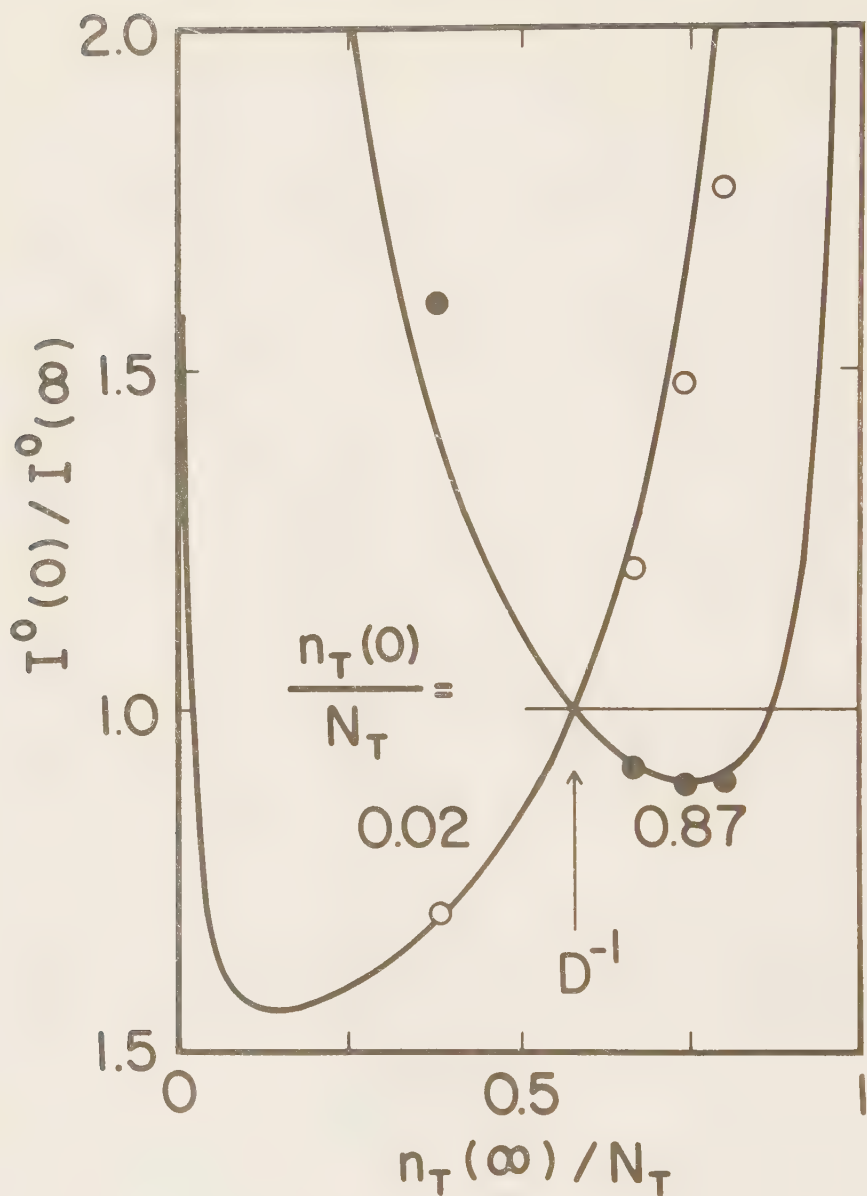


Fig 14. Fit of eq (16) to experimental data of the Si:Au_{acc} diode reverse biased by 25 V at 80 K. The initial occupancies were set by optical excitation with light of wavelengths 2.15 μm and 1.3 μm . The fit gives $D=1.72$.

be found, namely $n_T(\infty) = n_T(0)$ and $n_T(\infty)/N_T = D^{-1}$. In a diagram where the axes display the initial and final state occupancies (Fig 13) four regions separated by the two solutions can be marked, in which the initial to final current ratio is either larger or smaller than one. If the initial steady state occupancy is kept constant and the transient waveform is observed as a function of the final occupancy, the D-factor can be estimated. This was done for two cases and the results are shown in Fig 14. Also shown are the numerical fits of eq (16) to the experimental data, and from these the actual D-factor was deduced to be 1.72.

V. ELIMINATION OF DISPLACEMENT CURRENTS

When trap charges are altered in the transition region of a diode resulting in a current transient, a part of the excited charge builds up the displacement current that is responsible for the redistribution of space charge, which in turn can be detected as a capacitance change. If the capacitance instead is kept constant by a feed-back circuit no charge is needed for space charge redistribution. Then all excited charge will contribute to the current measured in the outer circuit and no displacement current is formed. The D-factor will always equal one under those conditions.

The necessity to measure current and capacitance at the same time is a technical problem. The current meter (Keithley 427) and the capacitance meter (Boonton 72B) reduce the sensitivity of each other by inducing noise. However, this obstacle can be circumvented by using a switching system in combination with sample & hold circuits. A block diagram is displayed in Fig 15. The idea is to alternatively for short time intervals couple the two instruments in and out of the diode circuit. During uncoupling, the output signals are kept constant by the sample & hold circuits. The capacitance signal is fed back to a regulator that keeps the diode capacitance constant by adjusting the applied reverse voltage semicontinuously,

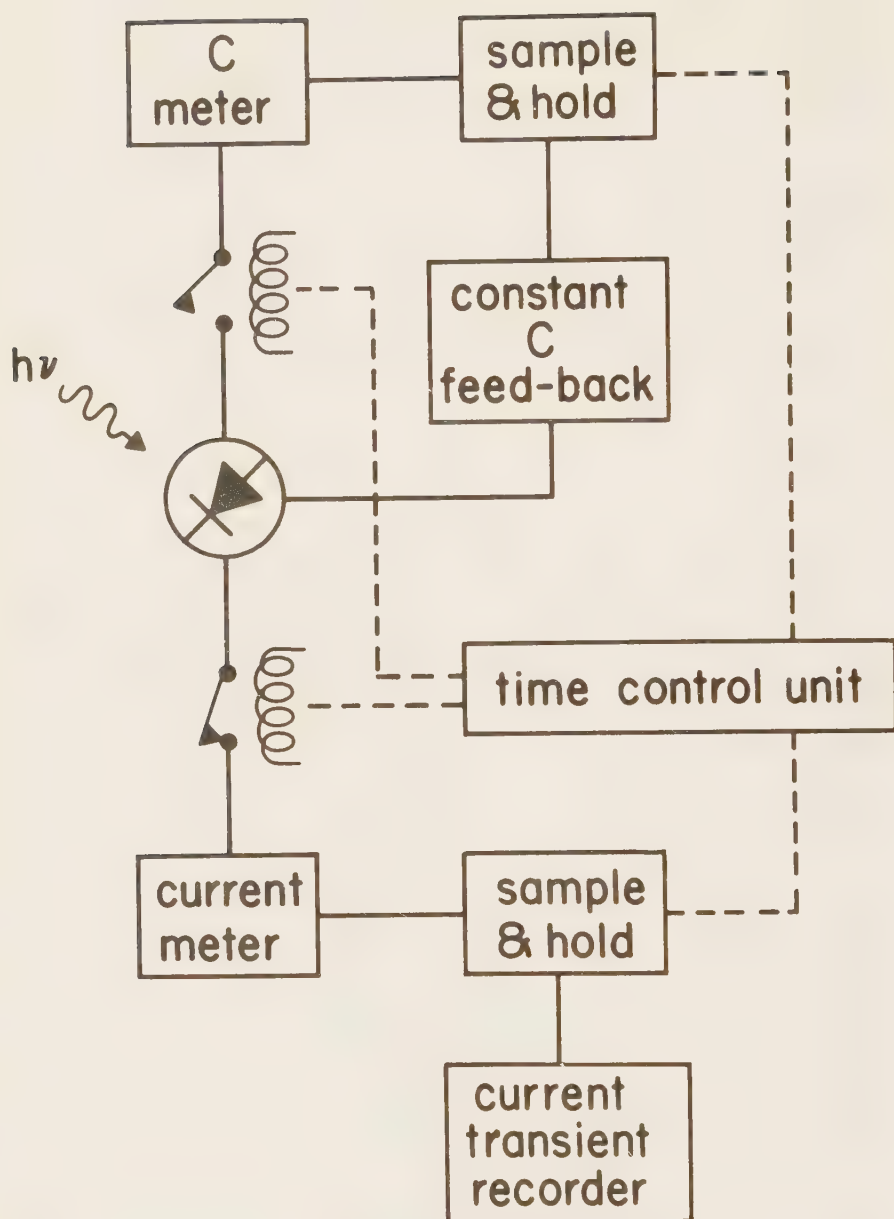


Fig 15; Block diagram of the setup described in the text for elimination of displacement currents.

i.e. adjusting periodically during each interval of capacitance measurement.

The Si:Au_{acc} system was used to test the setup for an optical transient. By simultaneously monitoring the current transient and the voltage transient taken from the output of the constant capacitance feed-back circuit, the D-factor can be calculated from

$$D = \frac{2\epsilon\epsilon_0 A \Delta V_r(\infty)}{(W-\lambda) I(0) \tau} \quad (17)$$

Both transients are shown in Fig 16 and the resulting D-factor was deduced to 1.02. Full occupancy was established in the initial state and the transient was induced by light of 0.67 eV photon energy. Eq (16) can be used to calculate the emission rate ratio, taking the initial and final current from Fig 16: $I(0)/I(\infty)=1.97$. We arrive at $e_n^0/e_p^0=1.01$ which is in agreement with the cross section ratio in Fig 4.

We used a time cycle of 163 ms. During this cycle the capacitance meter was measuring for 38 ms and the current meter for 97 ms. The recovery time of the current meter was about 25 ms. We believe that transients with time constants down to about 100 ms can be evaluated with our setup, using shorter time cycle. If the system is optimized by reducing the current meter recovery time it is possible to increase the range further.

The implication of this method is threefold. First, one is dealing with a well-defined D-factor, increasing the accuracy of the evaluation. Second, the signal increases since no excited carriers are lost for capacitance changes. Third, highly doped material can be used to increase the signal. The capacitance regulation assures that the transients will be exponential in spite of large changes in the space charge.

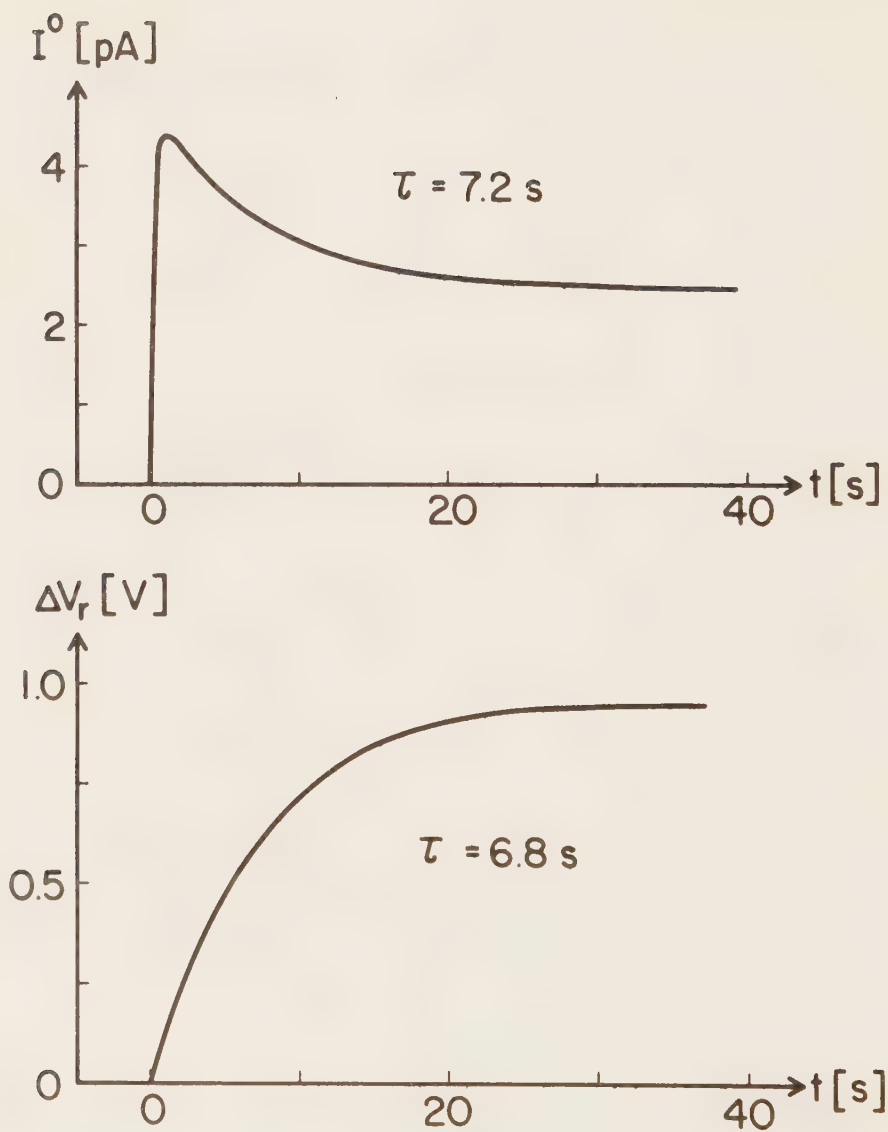


Fig 16. Optical current and voltage transients for light of photon energy 0.67 eV for Si:Au_{acc} under regulation conditions. The noise was about 10% of the maximum current.

VI. SUMMARY

The so called D-factor is a measure of the respective parts of the total number of excited charge that transport the measurable current and the displacement current in a transient experiment. We have demonstrated the nature of D for both thermal and optical experiments. The dependence on temperature, trap depth, applied reverse voltage, capture coefficients and active volume has been discussed. Strongest is the variation of D with the active volume which corresponds to the parameter in concentration profile experiments.

We have given the equations for theoretical derivation of the actual D-factor under different conditions, and described a simple technique for experimental determination of D. The method is built on measurements of the steady state generation current and the depletion region width as given by the inverse of the capacitance. For several cases comparison has been made between theory and experiments with good agreement.

Finally a technique is presented for elimination of displacement currents by keeping the diode capacitance constant. Then D is made equal to one resulting in increased transient amplitudes. Another advantage is that this method allows measurement of current transients in samples containing large concentrations of deep centers. The method was successfully tested. The present setup is capable of evaluating transients with time constants down to 100 ms, and it is possible to improve the measuring range further.

ACKNOWLEDGMENTS

The author is grateful to H G Grimmeiss for valuable discussions, B Skarstam for the sample preparation and K Nideborn and C Posselwhite for the realization of the current/capacitance switching system. This work was supported by the Swedish Board for Technical Development.

APPENDIX A

In this appendix the expressions for the edge region widths λ and μ is derived. We need first the rate equation that describes the processes shown in Fig 2:

$$\frac{dn_T}{dt} = (e_p + c_n n) N_T - (e_p + c_n n + e_n + c_p p) n_T \quad (18)$$

Here e_p and e_n are the sums of both optical and thermal emission rates

$$e_p = e_p^o + e_p^t, \quad e_n = e_n^o + e_n^t \quad (19)$$

but generally either the optical or the thermal processes are ruled out by the experimental conditions. The steady state electron occupancy is directly given by eq (18)

$$\frac{n_T(\infty)}{N_T} = \frac{e_p + c_n n}{e_p + c_n n + e_n + c_p p} \quad (20)$$

Depending on the part of the total depletion region which is under consideration some of the rates in eq (20) can be neglected. Especially electron capture outside the λ -region and hole capture outside the μ -region can be neglected. At the dividing-lines between the regions we require the occupancy to be the average between the occupancy in the transition region, $e_p/(e_p + e_n)$, and the occupancy within λ and μ which is one and zero respectively. We get for the free carrier concentrations at λ and $W-\mu$:

$$n(\lambda) = \frac{e_p + e_n}{c_n}, \quad p(W-\mu) = \frac{e_p + e_n}{c_p} \quad (21)$$

The free carrier concentrations as functions of the electrostatic potential are given by the Boltzmann equations assuming that the quasi Fermi levels are constant in the depletion region. The electrostatic potential is the parabolic solution to the Poisson equation. From these considerations we can deduce the position of the boundaries between the different regions

$$\lambda = \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} - kT \ln(c_n n(0)\tau) \right\}^{1/2} \quad (22)$$

$$\mu = W - \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \left[V_r + V_d - \frac{kT}{e} \ln(c_p p(W)\tau) \right] \right\}^{1/2} \quad (23)$$

In the optical case when the experiment is performed at a temperature where thermal emission can be neglected the time constant is

$$\tau^0 = (e_p^0 + e_n^0)^{-1} \quad (24)$$

and eq (21) can not be evaluated further. On the other hand, when only thermal processes are present we can use detailed balance relations to see the dependence of energy depth of the impurity state.

$$\lambda^t = \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \left[\frac{(F_n - E_T)_n}{e} - \frac{kT}{e} \ln\left(1 + \frac{e_p^t}{e_n^t}\right) \right] \right\}^{1/2} \quad (25)$$

$$\mu^t = W - \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \left[V_r + V_d - \frac{(E_T - F_p)_p}{e} + \frac{kT}{e} \ln\left(1 + \frac{e_n^t}{e_p^t}\right) \right] \right\}^{1/2} \quad (26)$$

$(F_n - E_T)_n$ and $(E_T - F_p)_p$ refer to the value in the neutral n- and p-type material respectively.

REFERENCES

1. H G Grimmeiss, Ann Rev Mater Sci 7, 341 (1977)
2. G L Miller, D V Lang and L C Kimerling,
Ann Rev Mater Sci 7, 377 (1977)
3. H G Grimmeiss and C Ovren, J Phys E 14, 1032 (1981)
4. S Braun and H G Grimmeiss, J Appl Phys 44,
2789 (1973)
5. H G Grimmeiss, L-Å Ledebø and E Meijer in
E Meijer, Thesis, Paper IV, Lund (1982)
6. O Engström, Thesis, Lund (1976)
7. S Braun and H G Grimmeiss, J Appl Phys 45,
2658 (1974)
8. O Engström and H G Grimmeiss, J Appl Phys 46,
831 (1975)
9. G Vincent, Appl Phys 23, 215 (1980)
10. D V Lang, H G Grimmeiss, E Meijer and M Jaros,
Phys Rev B22, 3917 (1980)
11. H G Grimmeiss, L-Å Ledebø and E Meijer, Appl Phys Lett
36, 307 (1980)

THE DYNAMICS OF CAPTURE FROM FREE-CARRIER TAILS IN DEPLETION
REGIONS AND ITS CONSEQUENCES IN JUNCTION EXPERIMENTS

H G Grimmeiss, L-Å Ledebo*) and E Meijer

Department of Solid State Physics, University of Lund, 220 07 Lund,
Sweden

*) Innovance AB, Magle Stora Kyrkogata 8, 223 50 Lund, Sweden

Exponentially decaying tails of free carriers extend from the neutral material into the depletion region of pn-junctions or Schottky barriers. In non-equilibrium, deep level impurities in the depletion region may readily capture free carriers from those tails. The strongly non-exponential time-dependence of the capture is here calculated and compared with experimental data. The appearance of the phenomenon is exemplified in a number of frequently used experiments. The capture is particularly important in deep level transient spectroscopy (DLTS), but appears as large effects in many other junction measurements with deep-level impurities.

Introduction

The depletion region is an important concept in semiconductor research and development. The physics of the junction is far from straight-forward. Often the depletion approximation is used when the junction is described, with the free-carrier concentration equal to zero within the space charge volume. This is however in many cases a poor approximation, particularly when deep-level impurities within the depletion region are studied. Inside the space charge volume, capture of free-carriers readily takes place from free-carrier tails in regions close to the boundaries of this volume. In thermal equilibrium a substantial fraction of the space charge volume is influenced by the presence of those tails. The importance of the edge regions has been pointed out before (1-4) and attempts have been made to use them constructively for the determination of activation energies of deep level impurities (5). The dynamics of the capture and its consequences has however not been considered and experimentally verified before. We describe here theoretically and experimentally the strongly non-exponential time-dependence of the capture from the tail. A simple model is used, which has been verified by a computer calculation, self-consistent with respect to potential.

We also describe how the time-dependent capture influences many frequently used measurements on deep level impurities. In DLTS-experiments (6), peaks with reversed signs and zero offsets may occur due to the free-carrier tails. In capture coefficient measurements, a substantial part of the signal may be due to the edge regions, and if this signal is mistakingly evaluated, an erroneous value for the capture coefficient is obtained. When minority carriers are injected in photo-capacitance investigations, tail-filling causes the capacitance to drift for a very long time, often obscuring the real signal. This phenomenon can be avoided by a simple pulsing sequence, improving the accuracy of the experiment by several orders of magnitude in many cases.

Time-dependence of the capture

The presence of the tails influences the occupancies of the levels in the edge regions. A possible situation at thermal equilibrium is shown in fig 1. In general the steady state occupancy of electrons

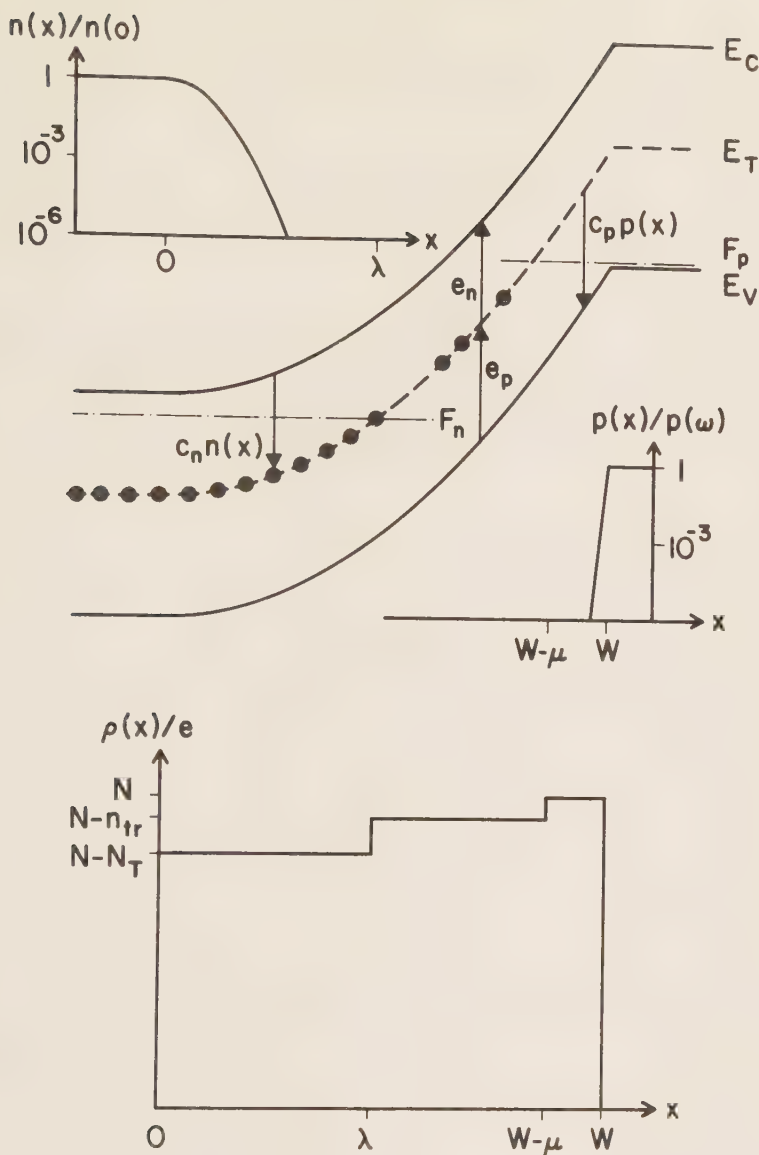


Fig 1. Energy band diagram for a reverse biased p^+n junction with a deep level impurity corresponding to the $\text{Si:Au}_{\text{acc}}$ system. Also shown are the relevant electron and hole transitions, the concentration of free carriers in the tails and the corresponding space charge distribution $\rho(x)$. The edge region widths λ and μ are the equilibrium values. N is the shallow donor concentration and n_{tr} is the concentration of centers occupied by electrons in the transition region.

$n_t(x, \infty)/N_T$ of the deep level with total concentration N_T is given by (4)

$$\frac{n_T(x, \infty)}{N_T} = \frac{e_p + c_n n(x)}{e_p + c_n n(x) + e_n + c_p p(x)} \quad (1)$$

where c_n and c_p are the capture coefficients for electrons and holes respectively. The emission rates e_n and e_p are the sums of the thermal and optical emission rates for electrons and holes respectively. The free electron concentration $n(x)$ and free hole concentration $p(x)$ as a function of distance are

$$\begin{aligned} n(x) &= n(0) \exp\left(-\frac{eV(x)}{kT}\right) \\ p(x) &= p(W) \exp\left(-\frac{e(V_r + V_d - V(x))}{kT}\right) \end{aligned} \quad (2)$$

where $V(x)$ is the solution to the Poisson equation for the electrostatic potential, V_d the diffusion voltage of the junction and V_r the applied reverse voltage. W is the corresponding width of the space charge region.

In thermal equilibrium the region of width λ in fig 1 is dominated by majority carrier capture and the occupancy equals one. In the region denoted by μ the occupancy is zero due to minority carrier capture. In the transition region, i.e. in the space charge volume between the two edge regions, the occupancy is $e_p/(e_p + e_n)$ as determined by emission. The resulting charge distribution in the space charge region is close to a staircase function. The boundaries at λ and $W - \mu$ do have a finite width, but since the free-carrier concentrations decrease very rapidly, it is a good approximation to consider them as abrupt. Equations for the equilibrium values of λ and μ have been calculated by Meijer (4), and were found to be:

$$\lambda = \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} - \frac{kT}{e} \ln(c_n n(0)\tau) \right\}^{1/2} \quad (3)$$

$$\mu = W - \left\{ \frac{2\epsilon\epsilon_0}{e(N-N_T)} \left[V_r + V_d - \frac{kT}{e} \ln(c_p p(W)\tau) \right] \right\}^{1/2}$$

where τ is the inverse sum of the emission rates.

If the steady-state occupancy in the edge regions are changed by external means, the system will return to steady-state by free-carrier capture from the tails after removal of the disturbance. This results in a transient capacitance signal for which we will derive the time-dependence. The equations for capture from the majority carrier tail and from the minority carrier tail in the respective edge regions are similar, and we will concentrate on majority carrier capture.

Assume an initial state at time zero where all deep centers throughout the space charge region are occupied by holes (fig 2a). Levels below the fermi level F_n will start to capture electrons (fig 2b), and the occupancy at each point x will increase towards a saturation value with a time-constant $\tau(x)$:

$$\tau(x) = \frac{1}{c_n n(x)} \quad (4)$$

The resulting capacitance transient is built up from occupancy changes in the full λ -region. (We denote the equilibrium values λ and μ without time parameter.) As the time-constant of eq (4) at normal temperatures is varying rapidly over many orders of magnitude within the edge region, the observed capacitance transient is strongly non-exponential. Because of the rapid variation with distance of the time-constant, it is reasonable to ascribe the capacitance change at time t to a small region where the time-constant for

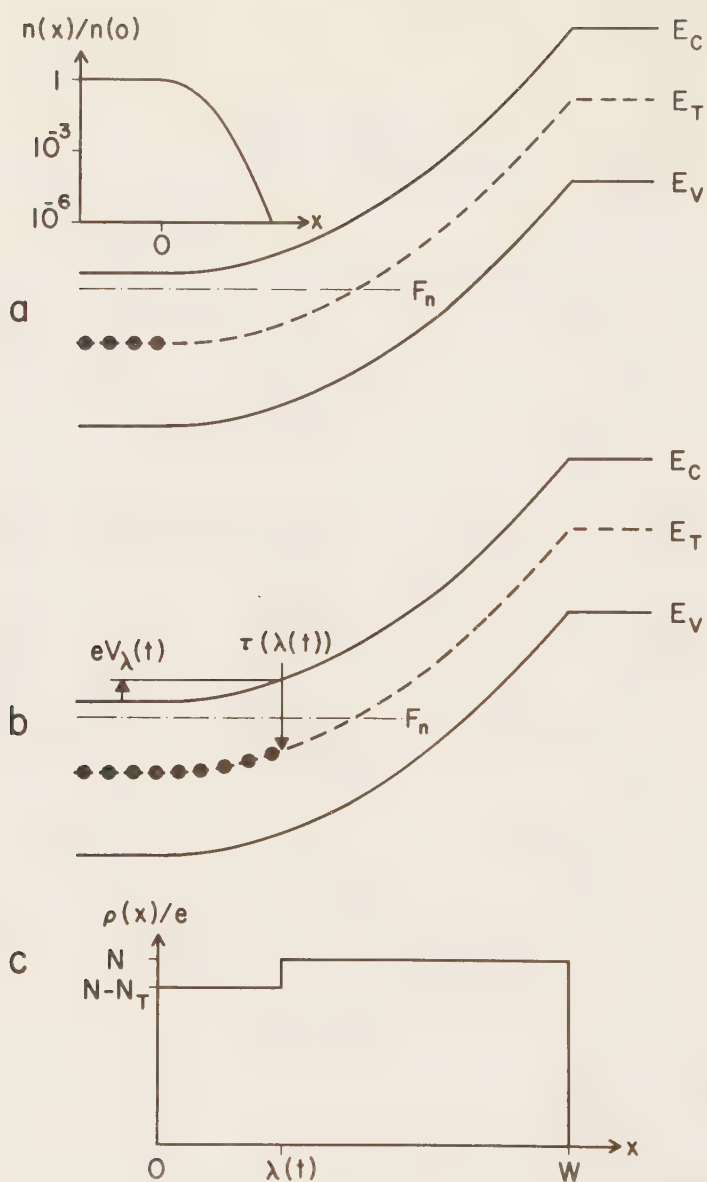


Fig 2. Energy band diagram a) defining $t=0$ after minority carrier injection, b) at $t>0$. c) Space charge distribution for the junction in b).

capture is close to t . The motivation is that in regions where the capture is faster, it has already gone to saturation, and in regions where the capture is slower, the variation is slow and the relative contribution to the capacitance transient negligible. We are thus led to the assumption that the distribution of the time-dependent space charge density is close to a staircase function as shown in fig 2c, with $\lambda(t)$ growing with time. Furthermore the transient component under observation at real time t takes place at $x = \lambda(t)$ and has a time constant proportional to t itself:

$$\tau(\lambda(t)) = \alpha t + t_0 \quad (5)$$

α is the proportionality constant and $t_0 = 1/c_n n(0)$, which is the capture time constant at $x = 0$.

$\lambda(t)$ corresponds to a band bending energy $eV_\lambda(t) = eV(\lambda(t))$ as shown in fig 2b. By using eq (2), (4) and (5) we get

$$eV_\lambda(t) = kT \ln(c_n n(0) \cdot (\alpha t + t_0)) \quad (6)$$

The time dependence of the capacitance $C(t)$ can be obtained by solving the Poisson equation for the space charge density distribution of fig 2c

$$C(t) = \frac{\epsilon \epsilon_0 A}{\frac{N_T}{N} \lambda(t) + \left\{ \frac{2\epsilon \epsilon_0}{eN} (V_r + V_d) - \frac{N_T}{N} \lambda(t)^2 \left(1 - \frac{N_T}{N}\right) \right\}^{1/2}} \quad (7)$$

where A is the diode area and

$$\lambda(t) = \left\{ \frac{2\epsilon \epsilon_0}{e(N - N_T)} V_\lambda(t) \right\}^{1/2} \quad (8)$$

The simple model described above has been compared to a selfconsistent computer calculation made by Grossmann (unpublished). The influence of the charge of the free-carrier tails and their influence on $V(x)$ was fully taken into account. The agreement with the simple

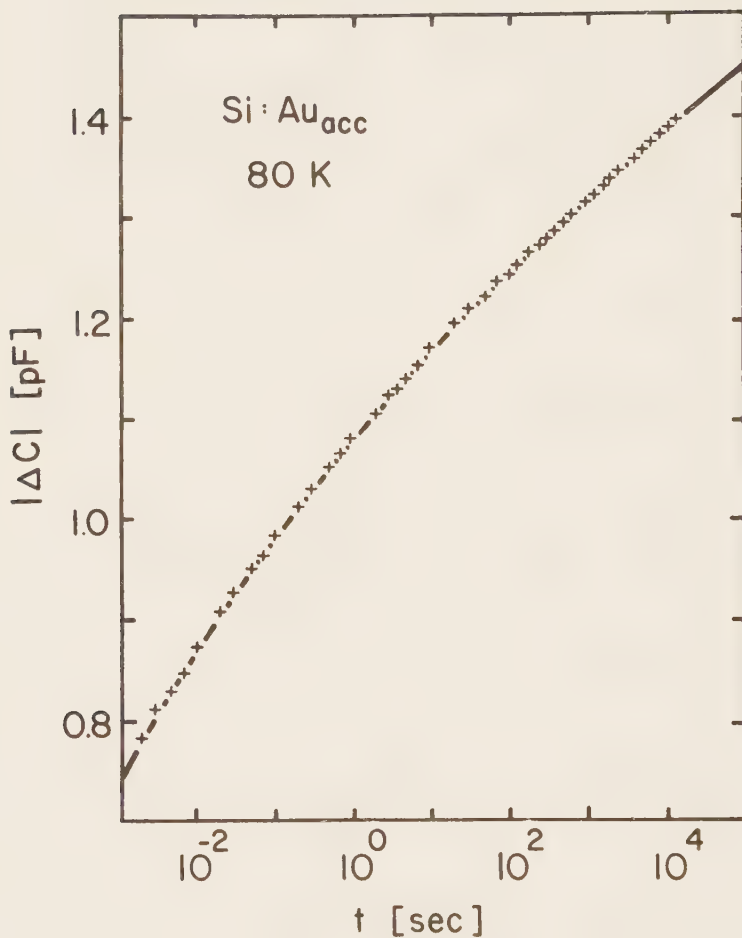


Fig 3. Capacitance change for a Au doped Si p⁺n junction at 80 K due to tail-capture by the Au_{acc}. The shallow donor concentration was $8 \cdot 10^{14} \text{ cm}^{-3}$ and the Au_{acc} concentration was $1 \cdot 10^{14} \text{ cm}^{-3}$. The solid line is a fit of eq (7). The capture cross section used was $\sigma_n = 0.5 \cdot 10^{-16} \text{ cm}^2$.

model above was excellent, justifying the continued use of our approximations. In the computer calculation $V_{\lambda}(t)$ could be determined by finding the position where the centers are half-occupied as a function of t . By comparing the computed data with eq (6), α was found to be 0.88.

The agreement between our model and experimental data is demonstrated in fig 3. The sample is a p^+n -diode of gold-doped silicon. Zero electron occupancy was established at high reverse bias at a temperature high enough for thermal emission to take place. After steady-state the sample was cooled to about 80 K. At $t=0$ the bias was lowered sufficiently much that the entire previous edge region with certainty is transformed into neutral material. This is exactly the situation discussed above. At times $t>0$ capture from the free electron tail results in a capacitance transient, which was recorded. The experimental data have been fitted with eq (7) in fig 3, with deep level concentration and capture coefficient as parameters. Obviously in small time intervals the capacitance change is closely logarithmic in time.

The parameters that mainly influence the time-dependence of the capture transients are deep level concentration N_T , reverse bias V_r , capture coefficient c_n and temperature T . The dependence of the first three is demonstrated in fig 4 - 6, where the rate of the capacitance change is calculated in a small time interval close to 1 sec, which is an experimentally relevant time. The capacitance transient is considerably more sensitive to the concentration of levels (fig 4) than to the value of the capture coefficient (fig 5). Unfortunately it is therefore not very easy to determine capture cross-sections by fitting the experimental capacitance variation unless the concentration of the level is known with high accuracy. Fig 6 reflects the decreasing importance of the edge region when the reverse bias is increased.

Experimental and theoretical capture transients at different temperatures are shown in fig 7. The initial condition was established by illumination with high-intensity light with photon energy 0.58 eV. This results in a steady-state electron occupancy for the gold-rela-

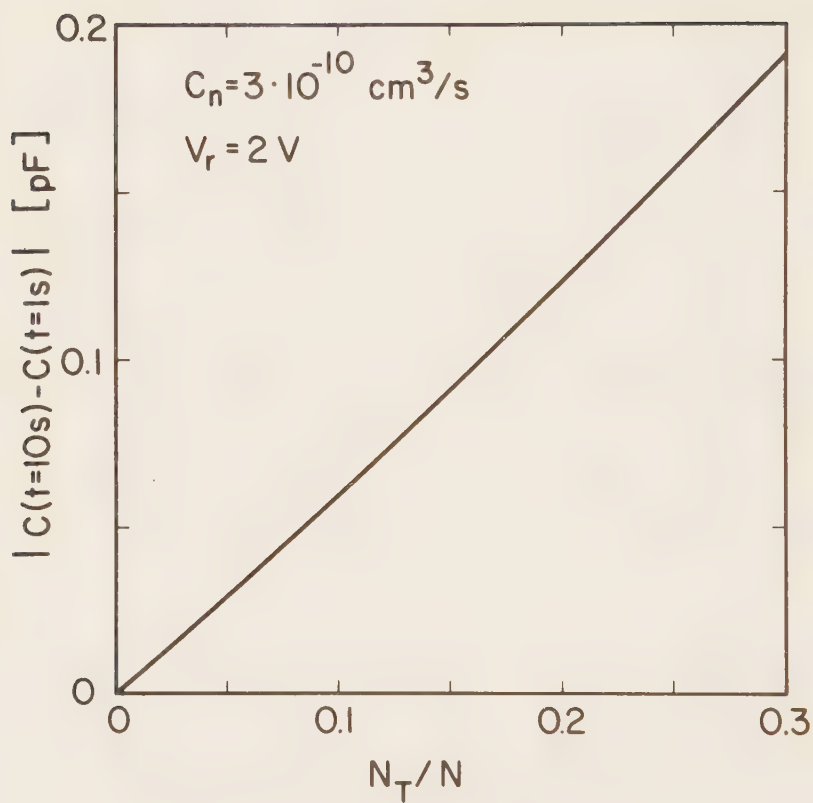


Fig 4. Calculated capacitance drift from 1 to 10 seconds as a function of compensation ratio N_T/N . The reverse bias is 2 V. Other parameters are the same as in the diode used for Fig 3.

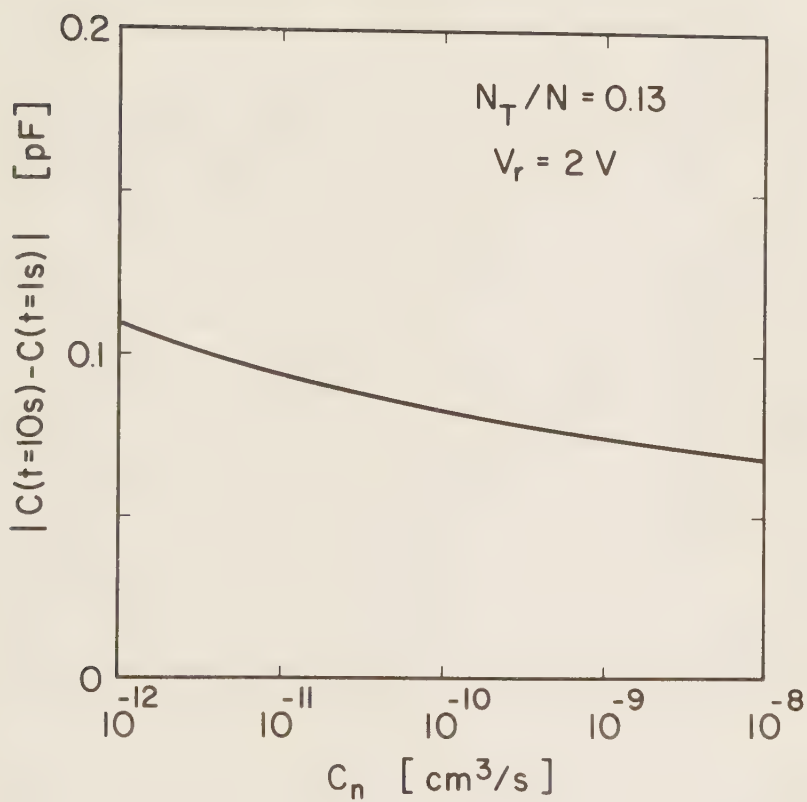


Fig 5. Calculated capacitance drift from 1 to 10 seconds as a function of electron capture cross section c_n .

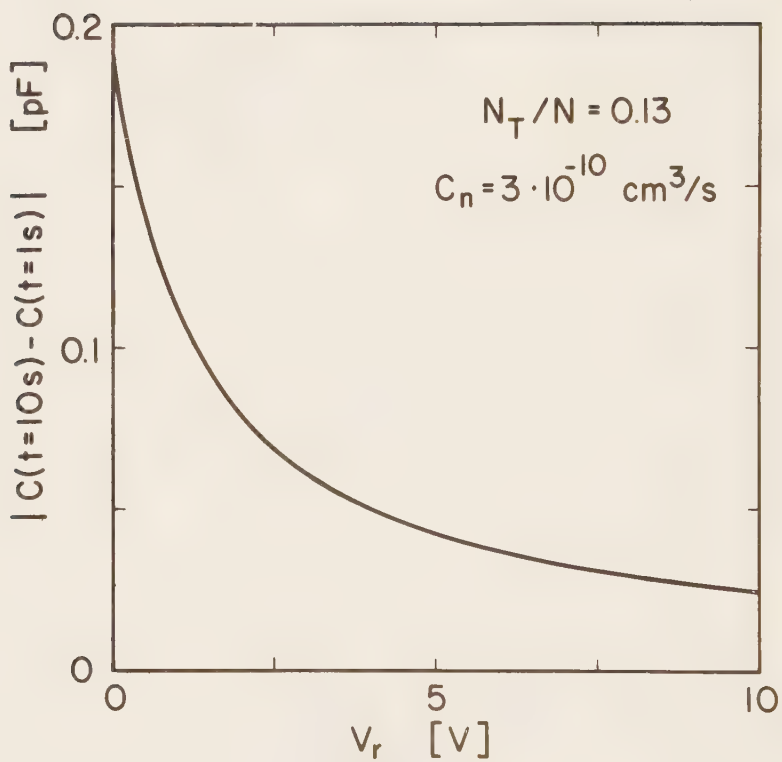


Fig 6. Calculated capacitance drift from 1 to 10 seconds as a function of applied reverse bias.

ted acceptor level close to zero (7) in the transition region and a small part of the edge region. The point of transition from occupancy one to occupancy zero is defined by (4)

$$c_n n(\lambda) = e_p^0 + e_n^0 \quad (9)$$

When steady-state is reached the light is switched off ($t=0$), and the capacitance transient recorded. t_0 now equals the time-constant for the optical emission.

The temperature dependence of the capture is rather complicated since several other parameters depend indirectly on the temperature. The electron capture cross section for the gold acceptor does not vary with temperature (7), but the thermal velocity does and therefore the capture coefficient as well. The diffusion voltage is affected by the temperature dependence of the Fermi level. Furthermore different initial conditions are obtained at different temperatures due to the temperature dependence of the optical emission rates (7). Our model was thus fitted to the experimental data of fig 7 by changing N_T/N from 0.128 to 0.11 and t_0 from 12 to 5 sec when the temperature was changed from 80 K to 185 K. The temperature dependence of the diffusion voltage and the capture coefficient were also taken into account.

The agreement between calculation and experiment in fig 7 is good with exception of the curve for 185 K, where saturation is observed in the experimental data. Saturation is indeed expected to occur when $\lambda(t)=\lambda(\infty)$. Capture further into the space charge region can not compete with the thermal emission, which has not been included in the model. The emission can be incorporated by numerical integration of the solution to the Poisson equation at different times. Consider the system described in fig 8a. By solving the rate equation for the concentration of levels occupied by electrons we get (4)

$$n_T(x,t) = n_T(x,\infty) - [n_T(x,\infty) - n_T(t=0)] e^{-\frac{t}{\tau(x)}} \quad (10)$$

where $\tau(x)^{-1} = c_n n(x) + e_p + e_n$ and

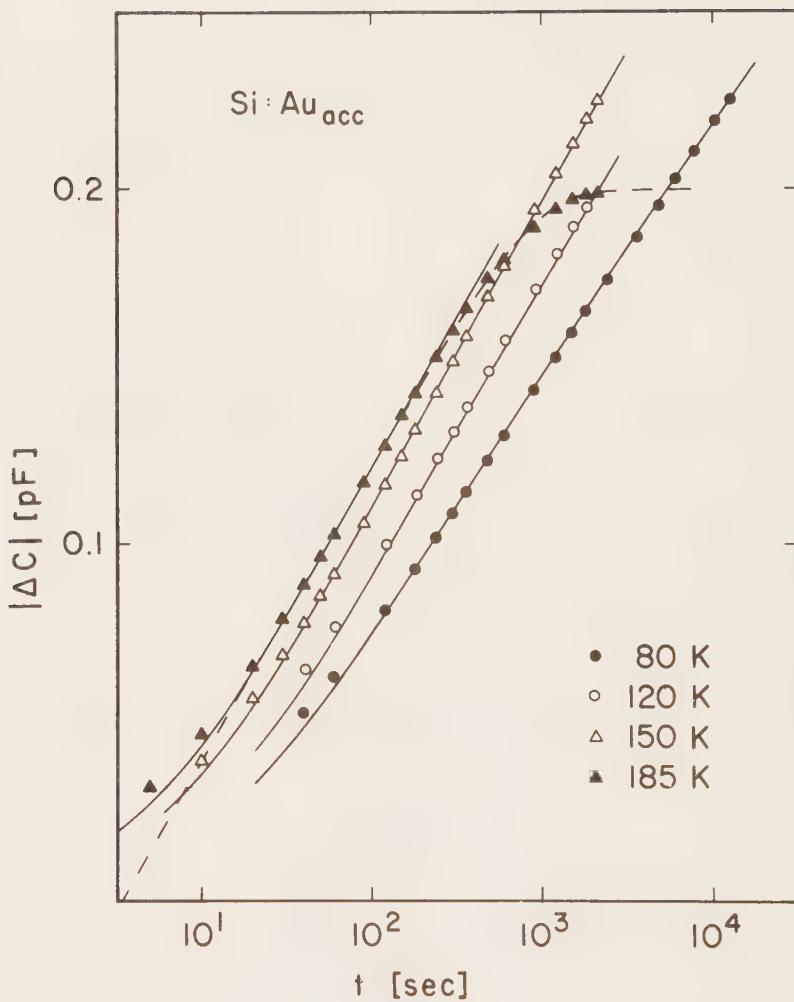


Fig 7. Capture transients at various temperatures, again for a Au doped Si p⁺n junction. The solid lines are calculations according to eq (7) as described in text and the dashed line is a fit of eq (13) to the 185 K data.

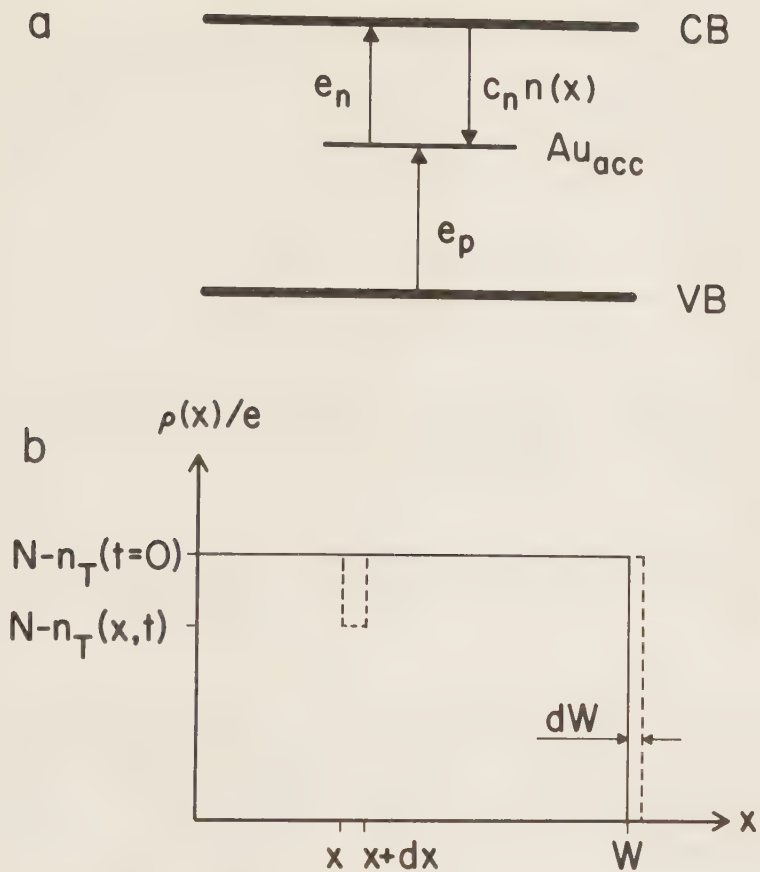


Fig 8. a) Energy band diagram showing electron and hole transitions in the depletion region positioned in n-type material. b) Distribution of the space charge density used for the derivation of eq (13). The solid line corresponds to the starting position and the dashed line describes the occupancy change in the interval dx at x , with a resulting change dW in the width of the space charge region.

$$n_T(x, \infty) = [e_p + c_n n(x)] \tau(x) N_T \quad (11)$$

The occupancy change in an infinitesimal volume between x and $x+dx$ results in a change dW of the width of the space charge region, as shown by the distribution of the density of charge in fig 8b. By solving the Poisson equation for time 0 and time t at constant reverse bias we get

$$dW(x, t) = \frac{n_T(x, t)}{N - n_T(t=0)} \left(1 - \frac{x}{W}\right) dx \quad (12)$$

The total change as a function of time is now obtained by integrating eq (12) over the whole space charge region. After transforming from occupancy to capacitance we get

$$|\Delta C(t)| = \frac{\epsilon \epsilon_0 A}{W^2} \int_0^W \frac{n_T(x, t)}{N - n_T(t=0)} \left(1 - \frac{x}{W}\right) dx \quad (13)$$

The dashed line in fig 7 is a fit of eq 13, numerically integrated. The parameters used were $e_n = 2 \cdot 10^{-3} \text{ s}^{-1}$ and $e_p = 6.5 \cdot 10^{-5} \text{ s}^{-1}$ in agreement with extrapolated experimental data (8). The integration procedure just described will prove to be important for the simulation of anomalous effects in DLTS spectra due to tail capture.

Tail capture in junction experiments

Junction barriers are frequently used for the characterization of deep level impurities in semiconductors. In many experiments capture from free-carrier tails gives a considerable capacitance signal. It is therefore often necessary to correct for the tail capture in order to properly evaluate the experiment. In the following we will discuss some important consequences in some types of measurements that are frequently used.

Optical transient spectroscopy is performed at low temperatures whe-

re thermal emission is negligible. If a minority carrier optical cross-section is to be measured, as for example σ_p^0 for a deep level impurity in a p^+n -junction, levels in the n -region must initially be filled by holes. This can either be done by using a suitable light source, or by electrical injection. In both cases hole-populated levels close to the neutral material tend to be refilled by electrons from the free-carrier tail when the light source or the current is switched off. This is exemplified in fig 9 for the so called B-level in a GaAs p^+n -junction. The transient caused by capture of carriers from the tail has the logarithmic time dependence demonstrated in fig 7, and at the low temperature used real steady-state is not obtained within the lifetime of the investigator. Often a drift in the capacitance is therefore by necessity accepted, with a decreased detectivity for optical excitation as a consequence. In order to avoid the drift we suggest the use of a clearing pulse as in fig 9, by which the edge region efficiently is filled. With proper choice of pulse amplitude and duration, upon restoration of the reverse bias a real steady-state is obtained, resulting in a considerably increased detectivity, even though the amplitude of the optical capacitance transient is slightly decreased.

Another severe implication of tail capture occurs in capture cross-section measurements by refilling methods. In such experiments unoccupied centers in the transition region are filled by short majority carrier pulses, and the resulting capacitance change is monitored as a function of total pulse width. During the bias pulse which normally is set to give zero bias, the major part of the depletion region is converted into neutral material. This part has a well-defined and constant capture rate $c_n(0)$. There is however still an edge region, where a slower capture occurs with a strongly varying time constant because of the variation of n with x . In a normal evaluation, where $\log \Delta C$ is plotted against time, the tail capture gives rise to a slowly varying capacitance, which may be interpreted as a second exponential that can be subtracted for evaluation of the cross-section. The absolute value of the cross-section obtained in this manner however is uncertain, as the final result depends on how the slow decay has been evaluated. The phenomenon is illustrated in fig 10, where the capture for the B-level in a GaAs p^+n -junction

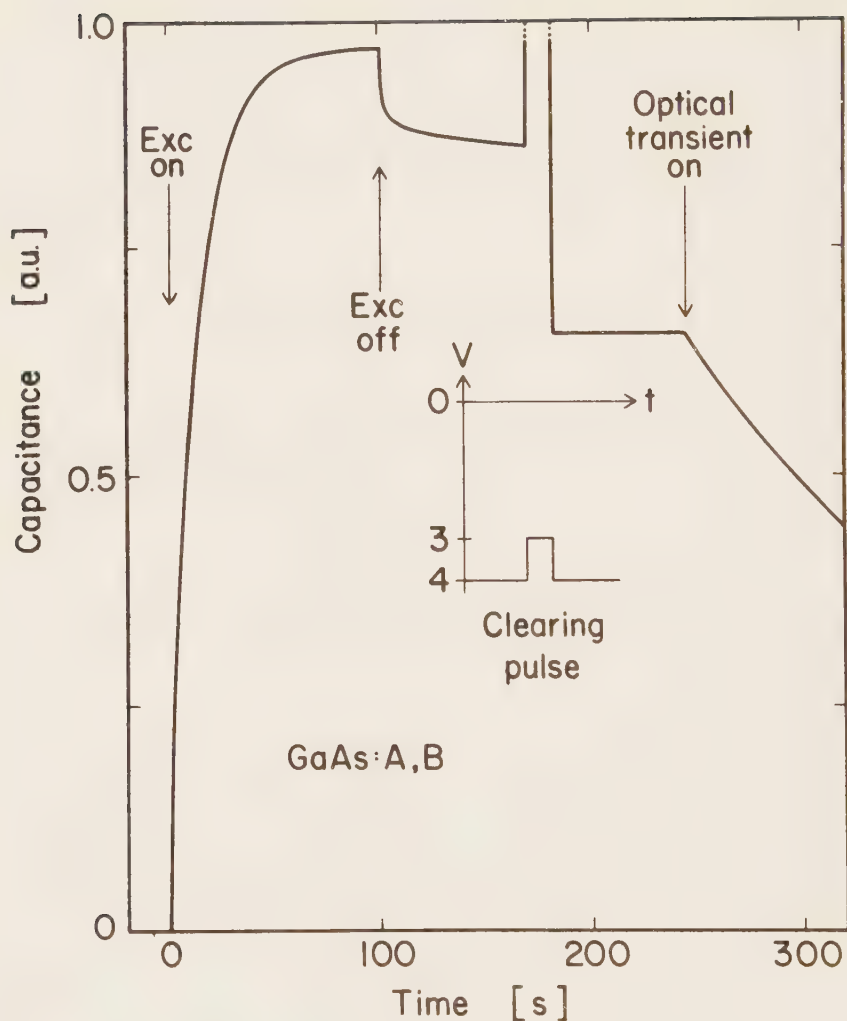


Fig 9. Capacitance transients during an experiment to determine the optical cross sections σ_p^o for the A and B levels in a GaAs p^+n junction. The initial hole occupancy is established by excitation with interband light. The electron tail-filling gives a large signal, which can be removed by a clearing pulse.

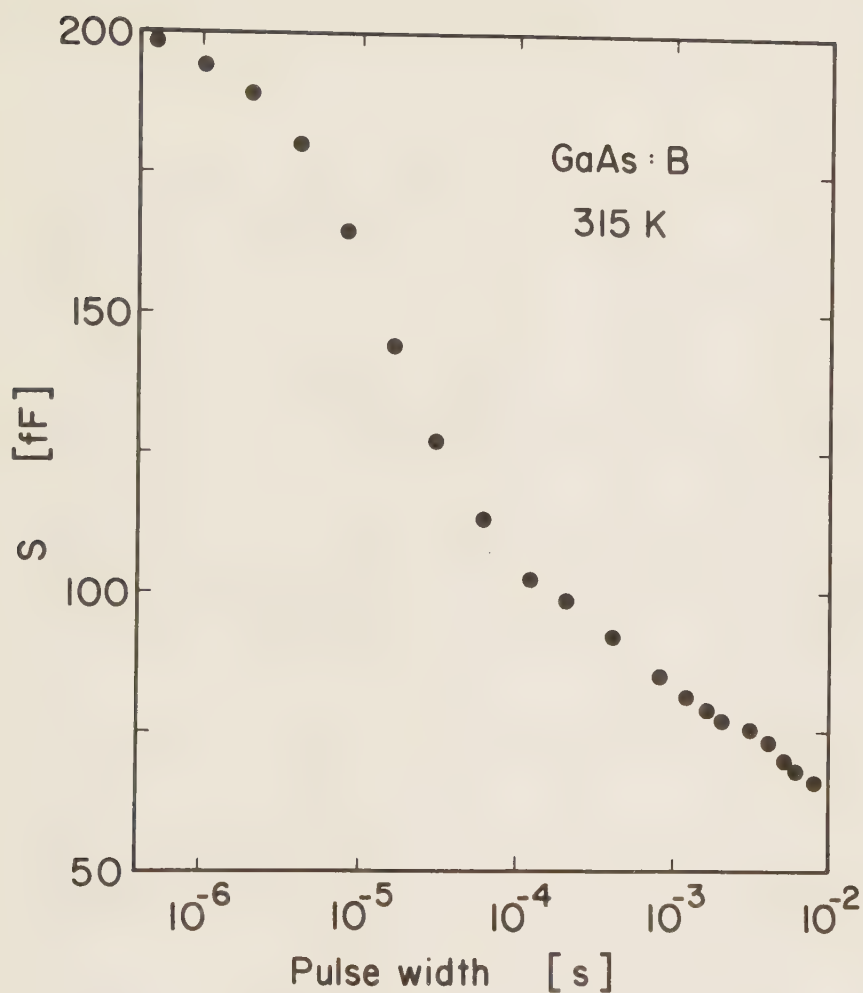


Fig 10. Experimental data for electron capture showing the importance of tail-filling in capture coefficient measurements. The DLTS technique was used. A refilling pulse resulting in full occupancy throughout the junction corresponds to $S=0$.

has been plotted as ΔC versus $\log t$. In this plot the tail-filling appears as a straight line, and when evaluating the data it is important not to use points in or close to this region. Alternatively the tail filling can be calculated and subtracted, but a recursive procedure then is necessary.

Another method to separate tail-capture from bulk capture has been suggested by Zylbersztejn (9). The slower contribution from tail filling is separated from the faster bulk contribution by observing the form of the transient as a function of reverse bias. The method however involves substantial experimental work, and the separation criterion is difficult to determine with accuracy. The problem of tail-filling in capture coefficient measurements can however be substantially reduced by the use of a Schottky diode. If the level lies in the lower half of the bandgap, the hole population must be obtained optically. Then by letting the bias pulse go into the forward direction sufficiently much to cause a near flat-band condition, the tail region is efficiently decreased. This procedure can unfortunately not in general be used in a pn-junction because of the electrical injection of minority carriers at forward bias.

Noras et al have pointed out the existence of rapid contributions in the beginning of the emission transients, making the evaluation of time constants difficult (3). However, only none or very small reverse biases were considered. The rapid contribution is easily understood, since the time constant at any point x in the barrier is the inverse sum of all the rates, i.e.

$$\tau(x) = (e_p + e_n + c_n n(x) + c_p p(x))^{-1}.$$

The time constant is thus smaller in regions where capture can occur. The free-carrier concentration however influences the amplitude of the change in the occupancy, and only in very narrow regions close to λ and $W - \mu$ do we get any contribution to the emission transient. The effect is therefore small in junctions that are reverse biased, and is thus normally not important.

The possibility to obtain trap binding energies from capacitance measurements at a single temperature was pointed out by Bleicher and Lange (10). The idea is to experimentally determine the equilibrium

value of λ , calculate the corresponding band bending energy eV_λ according to eq (6) and add the Fermi level position relative to the band. Bleicher and Lange determined λ by observing the time dependence of the capacitance at different biases. Another way to analyse C-V characteristics to get λ was suggested by Majerfeld et al (5). The same technique has been used in a number of later investigations (11-13), and is based on plotting C^{-2} versus V_r , first when all centers in the entire space charge region are occupied, then when only those in the edge region are occupied. λ can be found from the voltage differences in the two cases at constant capacitance, or from the difference of C^{-2} at constant bias as a function of C^{-1} . For the analysis to give a correct answer it is however necessary to make sure that the value of λ obtained is the equilibrium value (2). If this condition is not satisfied, as in the work by Majerfeld et al (5), serious misinterpretation of the energy position results. Using our model for the time-dependence of the tail-filling we can readily demonstrate the problem. Calculated $C^{-2} - V_r$ plots are shown in fig 11 for the so-called EL2 level in GaAs at 80 K. Full occupancy is easily obtained experimentally at low temperatures, but to get equilibrium with the centers occupied only in the edge region requires a time of the order of about 10^{38} sec at each value of the reverse bias. An apparent steady-state value is obtained rather fast, and the difference between waiting 1 ms or 24 hours is small. The value of λ obtained in this way is therefore rather a measure of the capture-cross section than of the binding energy of the level investigated. If the temperature is increased so that emission starts to be effective, the plotting technique suggested by Majerfeld et al (5) can however be used. In this case it is only necessary to wait for equilibrium for a time of the order of the time-constant for thermal emission. The data corresponding to full occupancy are calculated from the amplitudes of thermal transients after a saturating refilling pulse as a function of reverse bias. Measurements with false equilibrium and with real equilibrium are shown in fig 12. At 80 K we get the nonequilibrium value $eV_\lambda (t_{\text{wait}} = 1 \text{ min}) = 0.17 \text{ eV}$, whereas at room temperature the equilibrium value corrected for the Fermi level energy position yields $E_T = 0.72 \text{ eV}$ in good agreement with independent optical and thermal investigations.

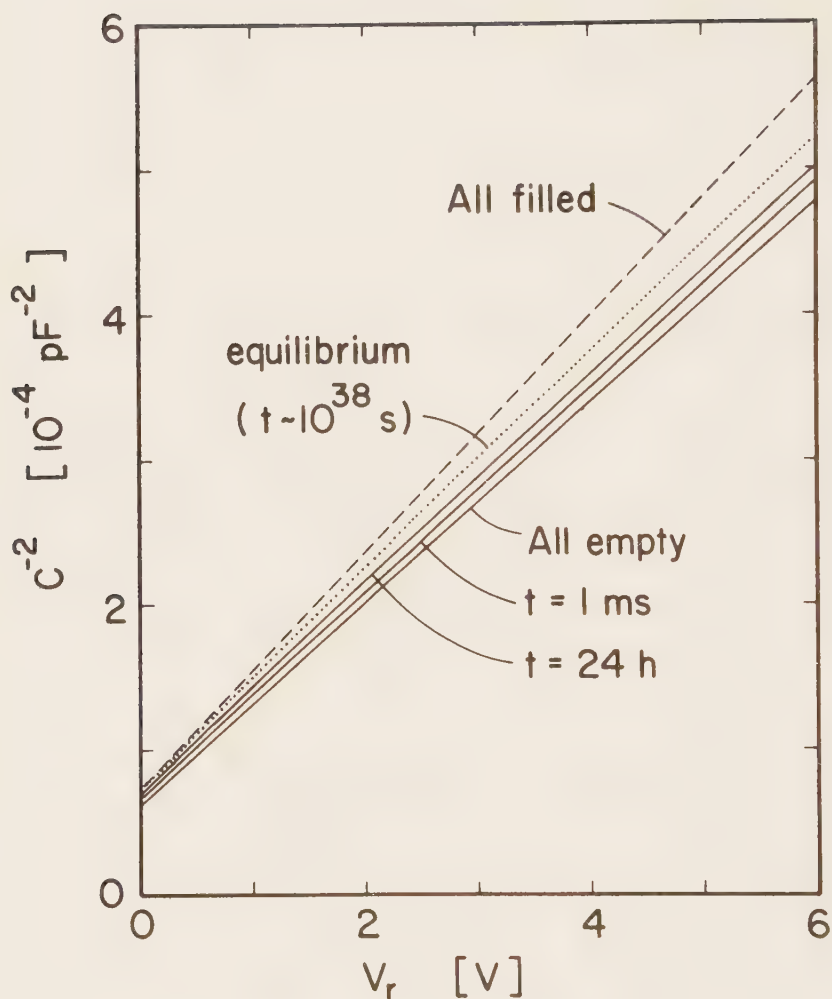


Fig 11. C-V characteristics calculated by eq (7) for a GaAs Schottky diode containing EL2-centers ($N_T=0.15N$, $T=80K$). The dashed line corresponds to all centers being occupied. The solid lines corresponds to occupied centers in the time dependent λ -region at $t=0$, 1 ms and 24 h. The dotted line refers to the equilibrium situation.

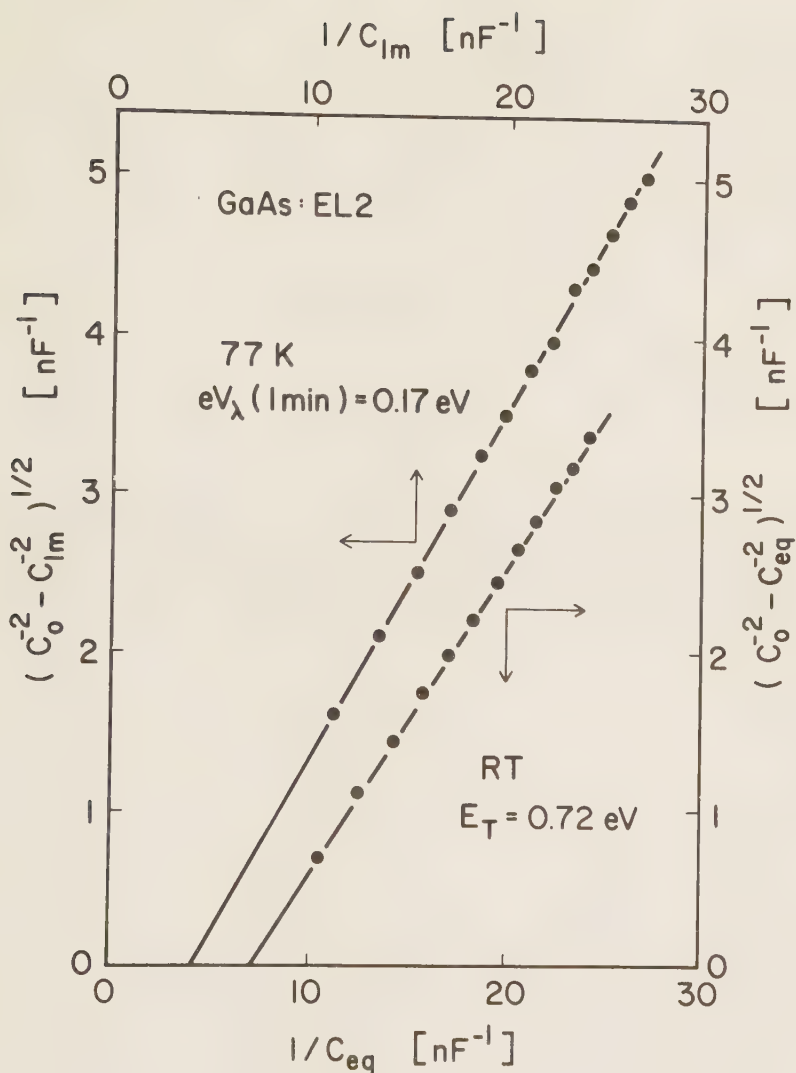


Fig 12. Determination of λ as described in text. C_o is the capacitance for full occupancy. C_{eq} corresponds to all centers in the equilibrium edge region being occupied, and C_{lm} is the capacitance after one minute of waiting time at 80 K. We used a Schottky diode with $N = 2.6 \cdot 10^{15} \text{ cm}^{-3}$, $N_T = 0.04N$, $A = 0.79 \text{ mm}^2$, $V_d = 0.9 \text{ V}$ and $c_n = 2.3 \cdot 10^{-10} \text{ cm}^3/\text{s}$.

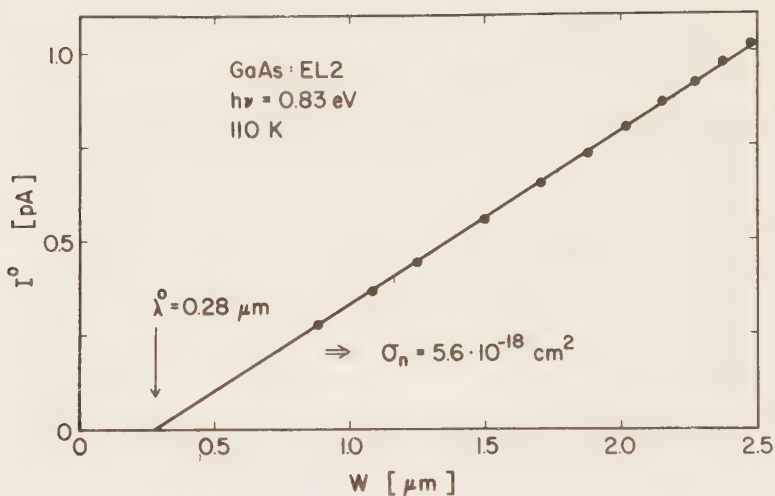


Fig 13. Optical steady state current versus space charge width W . The optical emission rate was 0.31 s^{-1} and λ^0 is obtained as the intercept of the line with the W -axis. Eq (3) is used to calculate the capture cross section. A Schottky diode was used ($N=1.6 \cdot 10^{15} \text{ cm}^{-3}$).

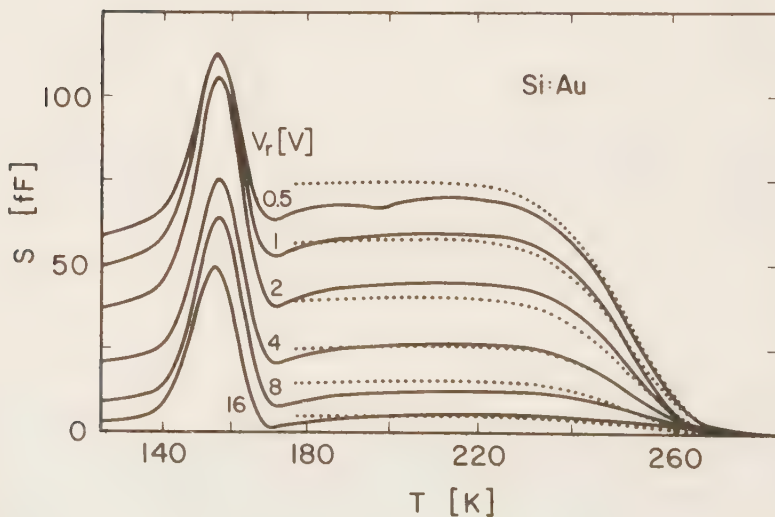


Fig 14. DLTS spectra for minority carrier injection showing transient capture signals of the Au_{acc} and the hole emission peak of the Au_{don} . The reverse bias has been varied and the spectra fitted with eq (13).¹⁵

The slow attainment of equilibrium can be used constructively to determine capture coefficients. At temperatures where thermal emission does not occur, optical one-step excitation can be used to empty the levels to a limit λ^0 (4), where the capture rate and the optical emission rate are equal. The optical emission rate can be measured independently, and by measuring λ^0 , the capture coefficient can be determined (14). The accuracy is however not very good since the capture coefficient depends exponentially on λ^0 as indicated in eq (3). A determination of the capture cross-section for EL 2 in GaAs by measuring λ^0 from a plot of optical steady-state current I^0 versus depletion region width W is shown in fig 13.

The capture from free-carrier tails can give rise to unexpected signals in DLTS spectra. We will here briefly describe this. Experimental information will be published elsewhere in more detail (15). In the search for minority carrier traps it is necessary to inject minority carriers into the junction. With suitable capture cross-sections, a positive DLTS-peak appears in the spectrum due to minority carrier emission subsequent to capture during the bias pulse. A minority carrier population will also be attained on traps in the edge region λ . After the bias pulse those levels will immediately start to capture majority carriers from the free-carrier tail. The corresponding capacitance transient gives the same sign in the DLTS-signal as a minority carrier trap. As the capture transient contains a wide spectrum of time constants irrespective of the temperature, the response from the DLTS equipment is an almost constant positive zero offset at low temperatures, decreasing towards zero for temperatures where thermal emission from the level starts to appear. The resulting shoulder-like spectrum is seen in fig 14 for the gold acceptor in a p^+n silicon junction. The peak in the spectrum corresponds to hole emission from the gold donor. The voltage dependence of the effect is illustrated in the figure, where also a theoretical fit of eq (13) is made.

The effects of the minority carrier tail are different, and come from minority carrier injection in a small volume close to the position $W - \mu$ even for low-amplitude bias pulses. A minority carrier trap present in this region therefore gives rise to a positive DLTS-peak instead of the normally expected negative majority carrier peak even for bias pulses that do not inject minority carriers. Nevertheless the resulting spectrum can be used for determination of both activation energies and concentrations for deep level impurities (15).

So far we have discussed only dynamical effects of the capture from the free-carrier tails. It may however be appropriate to mention the importance of the edge regions in some other cases. In a reverse biased junction the current often is a generation current. Braun and Grimmeiss (1) pointed out that this current does not get any contribution from the edge regions, because here two-step excitations cannot occur due to a rapid refilling from the tail. It has also been demonstrated (16) that previous conclusions about the electric field dependence of thermal emission rates for gold in silicon were incorrect due to the neglect of the edge regions.

Knowledge about the edge regions is also of vital importance in current transient measurements. The position and width of the active region determine the amount of the excited charge that contributes to the current detected in an outer circuit. This is often described in terms of the so-called D-factor (4). The evaluation of emission rates is quite sensitive to the value of D, and deep level profiling with current transients relies entirely on an accurate value of this factor.

Also deep level profiling with capacitance methods requires some thought about the edge regions. In a homogeneously doped sample the concentration in the depletion approximation is given by

$N_T = 2N \Delta C / C$, where ΔC is the change induced by altering the charge state of all centers in the entire depletion region and C is the absolute value of the diode capacitance. In this approximation $\Delta C / C$ is a constant independent of the reverse bias. Due to the edge regions the active volume is however at small reverse biases con-

siderably smaller than the total space charge region, and the capacitance change varies accordingly with reverse bias. An expression for a correction has been published recently (17). The correction can be avoided for $\Delta C \ll C$ by plotting $(\Delta C/C)^{1/2}$ versus $(V_r + V_d)^{-1/2}$ (3). A similar technique can be used if the junction contains large concentrations of deep level centers by using a feed-back loop and recording the voltage difference at constant capacitance at each reverse bias.

DLTS is another suitable technique for concentration profiling, with the bias pulse height as a parameter. The edge regions also in this case should be considered, which however is not normally done. It has recently been demonstrated how a correction can be made by adjusting the data to take the true active region into account (18).

Conclusion

The theoretical equations for free-carrier capture by deep level impurities in the space-charge region have been deduced, and with good agreement compared to experimental observations. A characteristic feature of the tail-filling is the logarithmic time-dependence, resulting in a very wide range of time-constants in corresponding capacitance transients. In many cases thermal equilibrium is not obtained within experimentally feasible times, even though the capacitance variation seemingly has finished. If the investigator does not realize that a false equilibrium is observed, great errors may result. An understanding of the tail-filling is particularly important in the analysis of DLTS-spectra, and for a proper evaluation of capture coefficients. In general the tail-filling is an important concept in "junction physics" with consequences for most deep-level impurity experiments.

Acknowledgment

We are grateful to B Skarstam who supplied the gold-doped silicon diodes used for this study, and to Zhan-Guo Wang for letting us use some of his data. We also acknowledge the financial support from the Swedish Board for Technical Development.

References

1. S Braun and H G Grimmeiss, J Appl Phys 44, 2789 (1973)
2. H G Grimmeiss, L-Å Ledebø and E Meijer, Appl Phys Lett 36, 307 (1980)
3. J M Noras and H R Szawelska, J Phys C 15, 2001 (1982)
4. E Meijer: Thesis paper II, Lund 1982
5. A Majerfeld and P K Bhattacharya, Appl Phys Lett 33, 259 (1980)
6. D V Lang, J Appl Phys 45, 3014, 3023 (1974)
7. D V Lang, H G Grimmeiss, E Meijer and M Jaroš, Phys Rev B22, 3917 (1980)
8. O Engström and H G Grimmeiss, J Appl Phys 46, 831 (1975)
9. A Zylbersztejn, Appl Phys Lett 33, 200 (1978)
10. M Bleicher and E Lange, Sol-State Electron 16, 375 (1973)
11. A Majerfeld, O Wada and A N M M Choudhury, Appl Phys Lett 33, 957 (1978)
12. P K Bhattacharya, A Majerfeld and A K Saxena, Inst Phys Conf Ser No 45, p 199 (1979)
13. O Wada, A Majerfeld and A N M M Choudhury, J Appl Phys 51, 423 (1980)
14. G Vincent, Appl Phys 23, 215 (1980)
15. E Meijer, L-Å Ledebø and Zhan-Guo Wang, in E Meijer: Thesis paper V, Lund 1982
16. S Braun and H G Grimmeiss, Solid State Commun 11, 1457 (1972)
17. D V Lang in Topics in Applied Physics 37, p 93, ed. P Bräunlich, Springer-Verlag (1979)
18. H G Grimmeiss, E Janzén, B Skarstam and A Lodding, J Appl Phys 51, 6238 (1980)



INFLUENCE FROM FREE-CARRIER TAILS IN DEEP LEVEL TRANSIENT SPECTROSCOPY (DLTS)

E Meijer, L-Å Ledebo*) and Zhan-Guo Wang**)

Department of Solid State Physics, University of Lund, 220 07 Lund, Sweden

*) Innovance AB, Magle Stora Kyrkogata 8, 223 50 Lund, Sweden

**) Permanent address: Institute of Semiconductors, Chinese Academy of Sciences, Peking, China

DLTS spectra of deep level impurities in semiconductors often display anomalies such as zero offsets, steps or peaks with reversed signs. For a correct interpretation of the spectra it is important to understand those features. They are here explained, and shown to be related to the presence of free-carrier tails which extend into the depletion region of a semiconductor junction. Gold-doped silicon and the so-called A and B levels in GaAs are chosen for illustration of the effects.

For the characterization of deep level impurities in semiconductors, DLTS (1) has proven to be very useful, particularly for rapid surveys. DLTS is also an important complement to optical investigations and to full-transient analysis for the determination of thermal activation energies. The ideal DLTS spectrum should display a single peak for each impurity level present in the depletion region. Additional features however often appear in real spectra. Temperature dependent zero offsets may be caused by trivial reasons such as sample dependent system transients or by the RC-time constant of the sample. Those phenomena are due to non-ideal instrumentation or samples, and are thus of little physical interest. More important and unavoidable are the signals arising from communication between the deep level impurity and the free-carrier tails in the depletion region. The importance of those tails has been pointed out before (2-5). The dynamics of the capture from the free-carrier tails has been calculated analytically (6), and the approximations used have been verified by a computer calculation, self-consistent with respect to electrostatic potential (7).

In a one-sided junction there is a majority carrier tail extending from the neutral material into the space charge region (fig 1), and a minority carrier tail extending into the space charge region from the metal contact in a Schottky diode or from the highly-doped side of a pn-junction (fig 4). The majority carrier tail gives signal due to majority carrier capture subsequent to minority carrier injection. The effect from the minority carrier tail is instead caused by minority carrier emission after capture from this tail during the bias pulse. The contributions to the DLTS spectra are quite different in those two cases.

We start by discussing the effects of the majority carrier tail, and for the experiments we have used a gold-doped silicon p^+n -junction. It is well-known that diffusion by gold in silicon introduces one acceptor level at about $0.6 + E_V$ eV, and one donor level at about $0.35 + E_V$ eV. To get any signal from the donor in a p^+n -junction, we must use hole injection by a forward bias pulse with a rapid back flank to avoid electron capture.

At sufficiently high injection level the volume in which the acceptor is filled with holes will extend further into the neutral material than the depletion region under reverse bias. When the reverse bias is restored, capture of electrons will rapidly take place in the neutral material. In the depletion region, the capture rate is determined by the free-carrier tail extending from the n-type neutral material as described in fig 1.

The DLTS-spectrum for simple injection is shown in fig 2, curve a. The peak at about 160 K corresponds to hole emission from the donor. No peak is seen from the acceptor because this level is in the upper half of the bandgap. (The experimentally determined ratio $e_n/e_p = 7.5$ at 260 K (8) should lead to a small negative peak; that no such peak is detected is evidence that we have not managed to get a complete hole occupancy.) At temperatures below about 260 K where the acceptor peak is expected we however see a large offset. This offset disappears if a small clearing pulse is applied as in fig 2, curve b. The clearing pulse fills the acceptor with electrons in a small region close to the neutral material, which removes the offset (and causes a low amplitude acceptor peak due to electron emission). For reference, in curve c the spectrum is taken only with majority carrier injection, displaying a totally normal DLTS signal from the acceptor.

We will now demonstrate that the offset in curve 2a is due to electron capture from the free-carrier tail by the acceptor. The free-carrier concentration $n(x)$ decreases exponentially with the potential in the depletion region:

$$n(x) = n(0) \exp\left(-\frac{eV(x)}{kT}\right) \quad (1)$$

where $n(0)$ is the free electron concentration in the neutral material and $eV(x)$ the band bending energy. The time-constant τ for capture of electrons from the tail by the empty acceptor level is

$$\tau(x) = \frac{1}{c_n n(x)} \quad (2)$$

c_n is the electron capture coefficient. Because of the exponential

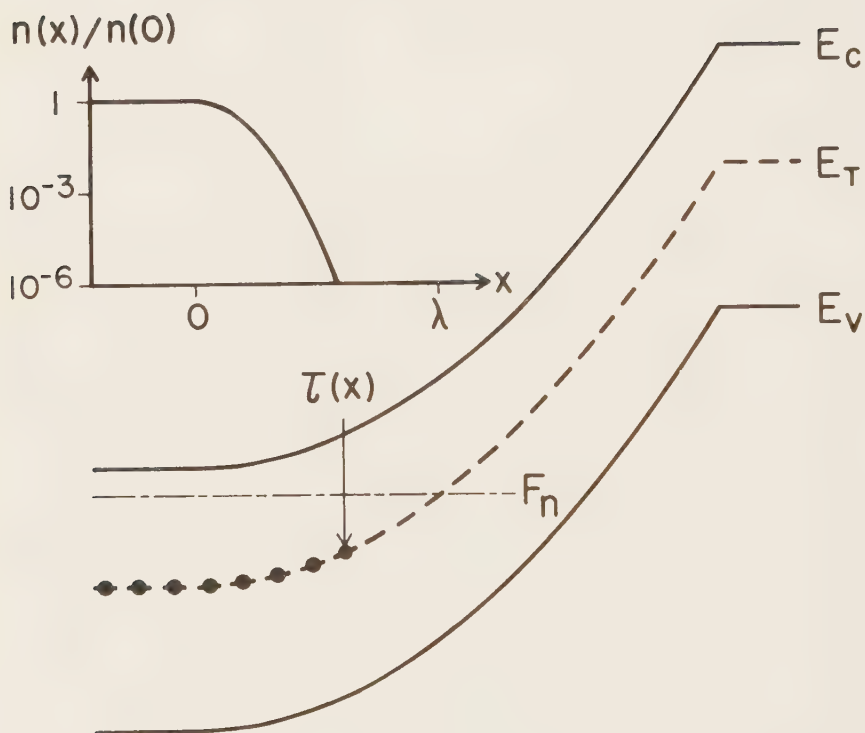


Fig 1. Band diagram of a p^+n junction. Following hole injection, the levels below the Fermi level on the n-side approach equilibrium with a time constant $\tau(x)$ by capture of electrons from the electron tail. The concentration of electrons is schematically shown in the insert.

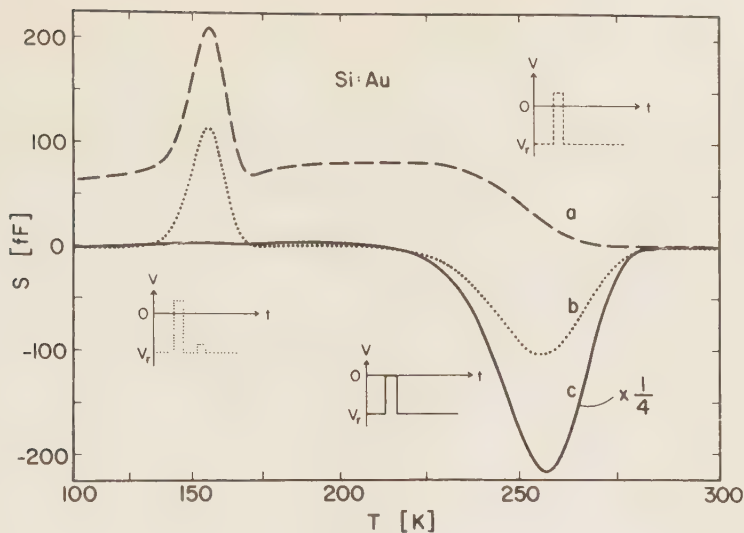


Fig 2. DLTS spectra for a gold doped silicon p^+n diode at different bias pulsing as indicated in the figure. The reverse bias was 4 V, the forward current during injection about 1 A/cm² and the cleaning pulse in case b had an amplitude of 0.6 V. The fall time of the back flank of the injection pulse was faster than 20 ns. The instrumentation used is described by Jansson et. al.¹²

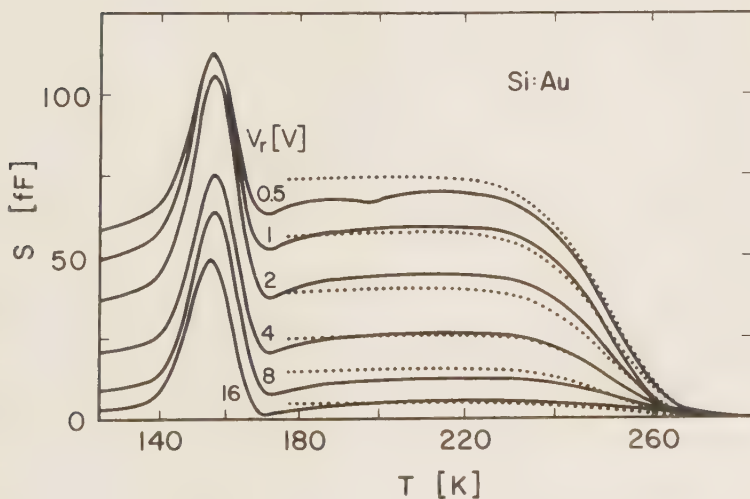


Fig 3. DLTS spectra for the sample described under Fig 2, taken at different reverse biases to demonstrate the bias dependence of the shoulder. The dotted lines is the calculation as described in text.

variation of $n(x)$, $\tau(x)$ will also vary exponentially with band bending. The capacitance transient during capture therefore contains time components from $1/c_n n(0)$ at the edge of the neutral material till $1/(2(e_n + e_p))$ at the position λ at the crossing between deep level and the fermi-level on the n-side. (e_n is the thermal emission rate for electrons for the gold acceptor, and e_p the thermal hole emission rate.) The time-dependent capacitance can be calculated by numerical integration of the solution to the Poisson equation (6):

$$|\Delta C(t)| = \frac{\epsilon \epsilon_0 A}{W^2} \int_0^W \frac{n_T(x, t)}{N - n_T(t=0)} \left(1 - \frac{x}{W} \right) dx \quad (3)$$

where the concentration of acceptors occupied by electrons $n_T(x, t)$ contains both the emission and the capture rates. The amplitude of the DLTS signal $S = \Delta C(t_1) - \Delta C(t_2)$ is easily simulated by using the time-dependence of eq (3). S is almost temperature-independent until the emission rate of electrons from the acceptor level starts to come close to the rate window of the DLTS equipment. This is quantified in fig 3, where the DLTS-spectrum for minority carrier injection is recorded at different reverse biases. The dotted line is the calculation with the capture cross-section $\sigma_n = 0.84 \cdot 10^{-16} \text{ cm}^2$. The only fitting parameter is the concentration of the acceptor. The value obtained was $0.31 \cdot 10^{14} \text{ cm}^{-3}$, in comparison with a concentration of $0.44 \cdot 10^{14} \text{ cm}^{-3}$ as determined by DLTS profiling.

In fig 2, curve b, the shoulder has disappeared. This is easily understood since the clearing pulse fills the acceptor levels close to the neutral material and in the depletion region at reverse bias. Upon restoration of the reverse bias no tail capture transient can therefore occur.

The phenomenon of the shoulder is not unique to gold-doped silicon. We have also seen it in injection modes in p^+n junctions for GaP:Cu, GaAs:Fe and GaAs:Cu. Generally the shoulder is expected as

soon as a level in the material captures minority carriers in injection, irrespective of whether the level is in the upper or lower half of the bandgap. As evident from fig 3 the effect can be decreased by using high reverse bias.

We now turn to the origin of peaks with reversed signs in majority carrier spectra. The effect is demonstrated in fig 5, where the signal from the A and B levels in GaAs has been recorded in a p^+n -junction. Both levels lie in the lower half of the bandgap (9), and give signal only by hole emission. The solid line is the normal DLTS-spectrum obtained by hole injection into the n-type depletion region. The two levels are due to the same defect (10). The levels therefore have the same concentration, which as expected is indicated by the similar amplitudes for the two peaks. However, also if a pulse is applied which definitely will not lead to any current and hence no holes are injected through the junction, the same peaks are seen, as demonstrated in the dashed curve in fig 5. This is at first confusing, since the sign of those peaks is contrary to that expected in majority carrier injection.

This is explained as follows: (See fig 4) On the n-side, close to the neutral material, the occupancy in thermal equilibrium is determined by the fermi level on the p-side where a region of extension μ is filled by holes. At zero bias all levels below the fermi level will be occupied by electrons. When reverse bias is applied, the slope of the impurity level energy position will increase close to the p-type material, and a region will be created below the p-type fermi level which is not in thermal equilibrium since levels in this region are filled with holes. Those holes will therefore be emitted with a time-constant characteristic for hole emission for this particular level, giving a DLTS-signal with the same sign and peak position as had the levels throughout the depletion region emitted holes after an injection pulse. During the bias pulse holes will be recaptured from the hole tail from the p-region. The time constants for recapture are given by equations similar to eq. 1 and 2. The signal of course has a smaller amplitude than at injection, since hole emission occurs only from a comparatively small volume. Also, at moderate bias pulse widths, the filling may not be complete since

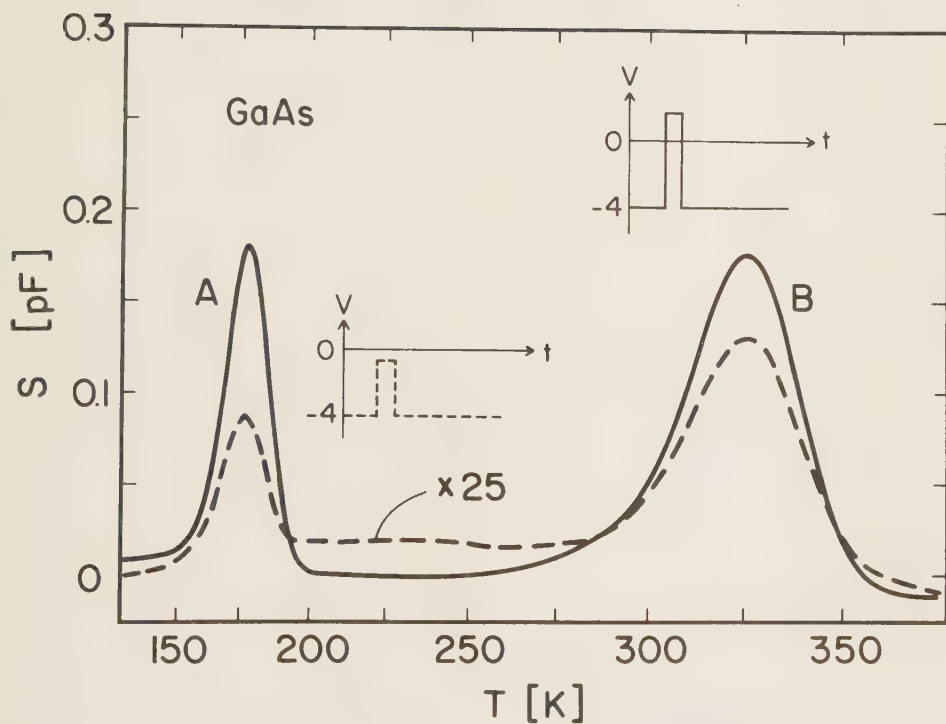


Fig 5. DLTS spectra for a GaAs p⁺n junction at different bias pulse conditions. The shallow doping of the n-side was $3 \cdot 10^{16} \text{ cm}^{-3}$, and the A and B levels had a concentration of about $2.5 \cdot 10^{14} \text{ cm}^{-3}$. The forward current at injection was about 1 A/cm^2

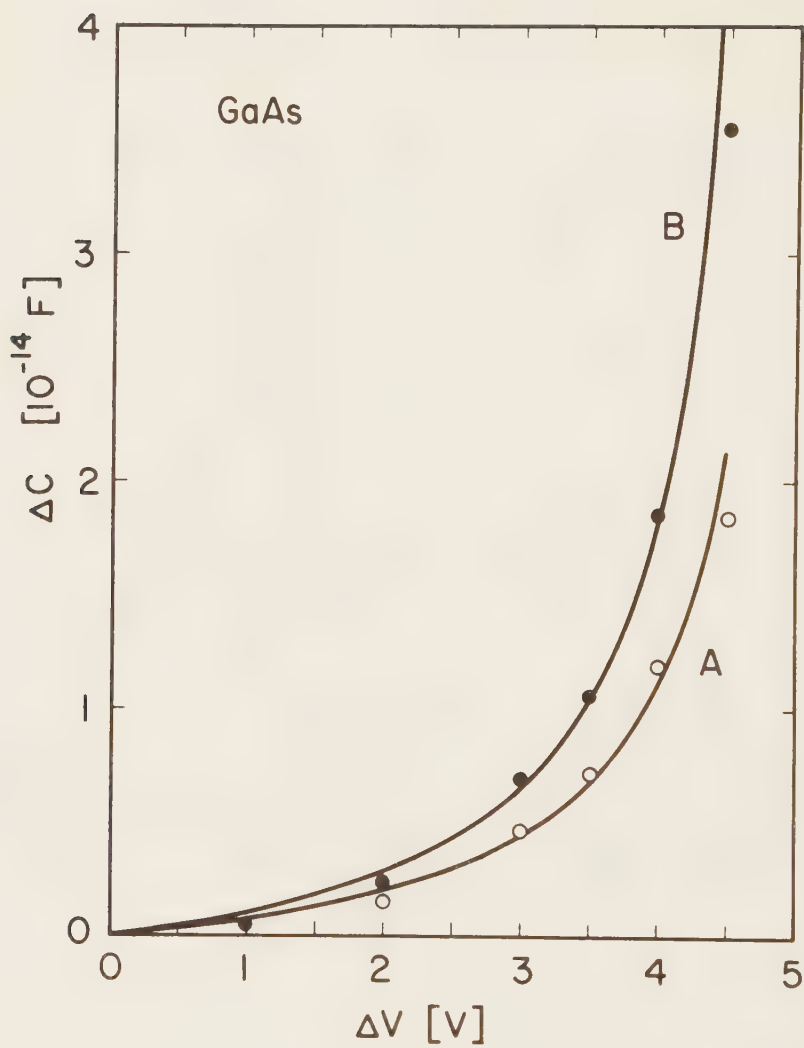


Fig 6. DLTS peak amplitude as a function of bias pulse amplitude at a constant reverse bias of 4 V. The points are the experimentally determined values from spectra such as the dashed spectrum in Fig 5. The solid line is the calculation according to eq (4).

thermal equilibrium is not attained. The ratio between peak amplitude and level concentration is different for different defects, partly because the volume of the active region depends on the level position. Furthermore, the capacitance sensitivity is strongly position dependent close to the metallurgical junction (11).

The peak amplitudes can be calculated by integrating the Poisson equation. We then get

$$|\Delta C| = \frac{\epsilon \epsilon_0 A}{2W(V_r)^3} \frac{N_T}{N} [\mu(V_p)^2 - \mu(V_r)^2] \quad (4)$$

where V_r is the reverse bias and $V_p = V_r - \Delta V$ the bias during the pulse. In fig 6, this equation is verified by studying the peak amplitude at varying bias pulses and a constant reverse bias. N_T has been used as a fitting parameter, but is within the experimental errors in agreement with the concentration of the levels as determined by optical capacitance transients. The calculation of which was needed for the fit is described in ref 12.

Reversed peaks are expected both in pn-junctions and in Schottky barriers for impurity levels in the lower half of the bandgap in n-type material and in the upper half in p-type material. In Schottky barriers the effect is less pronounced than in pn-junctions because of a smaller concentration of minority carriers in the edge region. We have however seen noticable effects in Schottky barriers on n-type material both for GaAs:Cu and GaAs:Fe. One reason for the appearance of the reversed peaks in those samples may be the high detectivity, as they were made by liquid phase epitaxy with very low concentrations of spurious defects.

This study was supported by the Swedish Board for Technical Development.

References

1. D. V. Lang, J. Appl. Phys. 45, 3014, 3023 (1974)
2. A. Zylbersztejn, Appl. Phys. Lett. 33, 200 (1978)
3. G. Vincent, Appl. Phys. 23, 215 (1980)
4. J. M. Noras and H. R. Szawelska, J. Phys. C 15, 2001 (1982)
5. H. G. Grimmeiss, L.-Å. Ledebø and E. Meijer, Appl. Phys. Lett. 36, 307 (1980)
6. H. G. Grimmeiss, L.-Å. Ledebø and E. Meijer in E. Meijer: Thesis paper IV, Lund 1982
7. G. Grossmann, unpublished
8. O. Engström and H. G. Grimmeiss, J. Appl. Phys. 46, 831 (1975)
9. Zhan-Guo Wang, L.-Å. Ledebø and H. G. Grimmeiss, unpublished
10. L.-Å. Ledebø and Zhan-Guo Wang, unpublished
11. D. V. Lang in Topics in Applied Physics, 37, 93 (1979), Springer-Verlag, Ed. P. Bräunlich
12. E. Meijer: Thesis paper II, Lund 1982
13. L. Jansson, V. Kumar, L.-Å. Ledebø and K. Nideborn, J. Phys. E 14, 464 (1981)

DEEP ENERGY LEVELS IN $\text{ZnS}_x\text{Se}_{1-x}$ ALLOYS

H G Grimmeiss and E Meijer

Department of Solid State Physics, University of Lund, Box 725,
S-220 07 LUND, Sweden

R Mach

Zentralinstitut für Elektronenphysik der Akademie der Wissenschaften der
DDR, Mohrenstrasse 40/41, DDR-1080 BERLIN, GDR

I Introduction

II - VI compounds and their alloys are widely used as phosphors. Their optical properties have been studied intensively during the last decades and, their luminescent properties in particular have been described in a great number of papers. Some of these alloys are of particular interest since their energy band gaps, E_g , allow optical emission in the whole visible spectral region. Such properties are of great interest for the development of optoelectronic devices, and potential host compounds are ZnS, ZnSe and $\text{ZnS}_x\text{Se}_{1-x}$ alloys ¹⁾. From an academic point of view mixed crystals are of special interest for studying disorder model systems. The simplest conditions for such a study are obtained when centers giving rise to localized states are investigated, since they may be influenced only by their nearest neighbours.

Cubic ZnS and ZnSe are similar in their properties with respect to their dielectric constants, band structures, lattice constants etc ²⁾. They are completely miscible in all compositions. The band gap variation when going from ZnSe to ZnS is about 1 eV.

The incorporation of foreign atoms in ZnS or ZnSe is often accompanied by other processes such as selfcompensation. In the case of donors, compensation occurs due to the formation of deep acceptors. These selfactivated (SA) centers act as radiative recombination centers and are responsible for the selfactivated emission ³⁻⁵⁾. The selfactivated center is found to be identical with the A-center ⁶⁻⁹⁾. The microscopic structure of the A-center, formed by a zinc vacancy and a shallow donor, has been revealed by electron spin resonance (ESR) measurements ¹⁰⁾. The shallow donor is either a halogen atom on a nearest anion site or a group III metal on a nearest zinc site. Such a center lacks one positive charge with respect to the lattice and acts therefore as a charge compensator for an ionized shallow donor. The center can optically be occupied by a hole and is then paramagnetic. In the case of the halogen A-center the hole is localized on the chalcogen atoms at the three remaining nearest anion sites. Owing to the overlap of the three equivalent chalcogen orbitals, a splitting into two states takes place. One of them is twofold degenerated. This degeneracy is lifted by the Jahn-Teller distortion and the unpaired hole is localized on one of the three distorted sites ¹⁰⁾. At elevated temperatures the hole is thermally activated and hopping occurs among these three sites ¹¹⁾. For the metal A-center the sites surrounding the zinc vacancy are not equivalent. The unpaired hole is always localized on the chalcogen atom which is farthest from the positively charged center ¹⁰⁾.

If the defect wavefunction is sufficiently localized, the halogen A-center can be regarded as a defect which is confined to the zinc vacancy and its nearest neighbours. Only four different configurations of the center are then possible in the $\text{ZnS}_x\text{Se}_{1-x}$ alloys since one of the four nearest neighbour sites is occupied by the halogen atom. The four possible

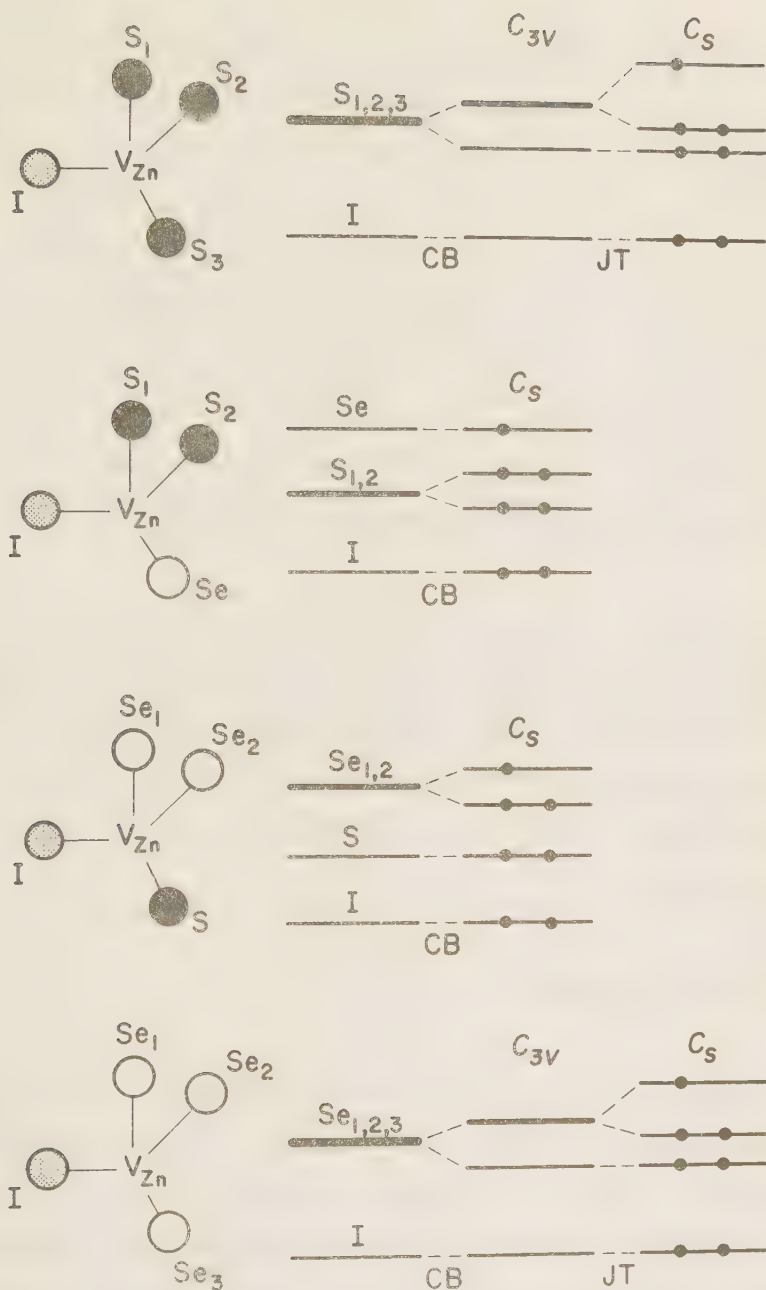


Fig 1. LCAO molecular orbital models for the four I-SA-centers. CB= chemical bond denotes the splitting due to overlap of atomic orbitals. The Jahn-Teller distortion is denoted by JT.

configurations are labelled as 3S-, 1Se-, 2Se- and 3Se center (Fig. 1). This model was first suggested by Fonger ¹²⁾, who used it together with statistical considerations to explain the behaviour of the selfactivated luminescence as a function of compensation. The relative occurrence of these centers is readily calculated if a random distribution of chalcogen atoms for any composition is assumed (Fig. 2). ESR ¹³⁾, optically detected magnetic resonance (ODMR) ¹⁴⁾ measurements and a recent study of photoluminescence spectra ¹⁵⁾ seem to confirm the existence of these centers, although other investigations ¹⁶⁾ performed on crystals of mid-range composition probably question the validity of the model.

The purpose of our study was to obtain further information on the electronic properties of the SA center in $\text{ZnS}_x\text{Se}_{1-x}$ alloys by measuring the photoionization cross section spectra of both electrons and holes under different experimental conditions. It is shown that these results together with luminescence data give very little information on the validity of the four center model.

II Sample Preparation

Single crystals of $\text{ZnS}_x\text{Se}_{1-x}$ alloys have been grown by the iodine vapour transport technique, as described previously ¹⁵⁾. The as-grown crystals are high-resistive, in spite of the fact that they contain a large amount of iodine. Extraction of foreign impurities was successfully performed on ZnSe by treating the crystals twice in high purity molten zinc ¹⁷⁾. Similar procedures were employed for purification of our $\text{ZnS}_x\text{Se}_{1-x}$ samples. Some samples were additionally doped with aluminum or copper. This was achieved by adding the desired metal to the zinc melt prior to the second treatment.

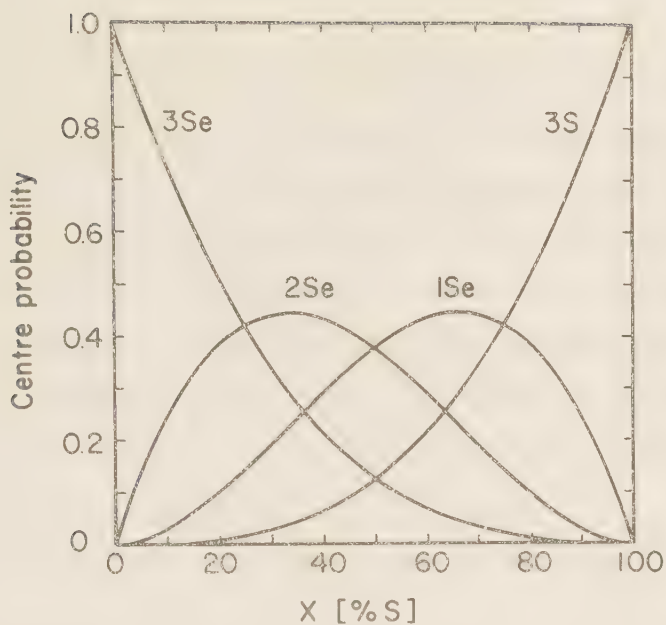


Fig 2. Statistical probabilities for finding SA-centers in $\text{ZnS}_x\text{Se}_{1-x}$ consisting of a Zn vacancy surrounded by an I atom on one chalcogen site and possible combinations of S and Se atoms on the three remaining sites.

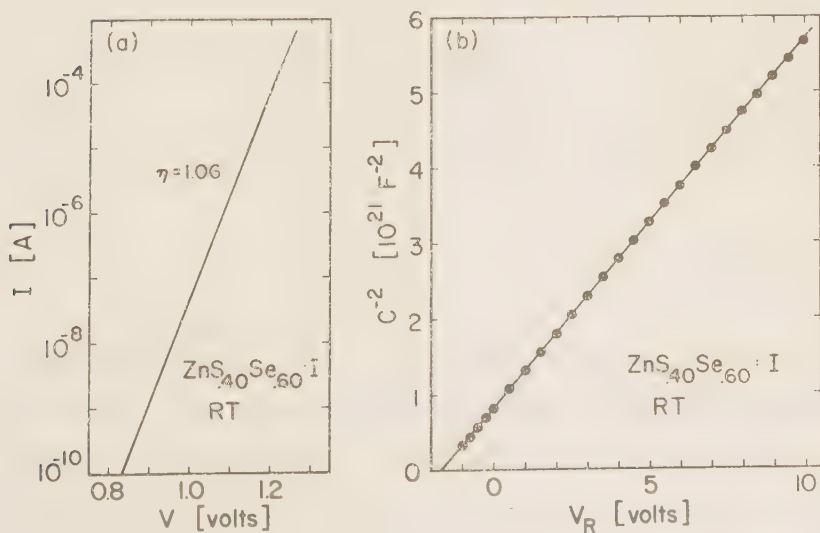


Fig 3. a) I-V, and b) C-V characteristics for a typical sample.

Each crystal was cleft into two pieces. One part was used for characterization by photoluminescence, Hall measurements and excitonic reflection spectroscopy¹⁵⁾. The second part was used for the fabrication of Schottky barriers. Ohmic and Schottky contacts were made on air-cleft crystals directly, since etching procedures were found to lead to formation of surface layers of high resistivity. The ohmic contacts were obtained by alloying indium pellets in streaming H_2 , and the rectifying gold contacts were vacuum deposited by evaporation.

III Characterization of Samples

All samples used in this investigation have been carefully examined with regard to composition, deep centers and the quality of the Schottky barrier. The composition, x , i.e. the percentage of sulfur in the chalcogen sublattice has been measured applying electron-excited X-ray analysis.

The quality of the Schottky barrier has been checked by measuring the voltage dependence of the dark current and capacitance. A typical $I - V$ characteristic is shown in Fig. 3a. It is readily seen that the ideality factor η as defined by the diode equation ($eV \gg kT$)

$$I = I_0 \exp \frac{eV}{\eta kT} \quad (1)$$

is very close to 1. In none of the diodes, was any detectable reverse or leakage current ($<10^{-13}$ A) observed for biases up to 10 V. The onset of the current and the series resistance, however, vary for different diodes due to the variation of the barrier height, eV_D , and the free carrier concentration in the bulk material, n , with composition. n was calculated from $C^{-2}-V$ plots (Fig. 3b) using a composition-dependent dielectric constant

TABLE 1 The free carrier concentration n and the diffusion voltage V_D at room temperature, determined from $C-V_R$ characteristics for all diodes used.

x (%S)	Dopant	n (10^{16} cm^{-3})	V_D (V)	η
9	I	67.9	2.00	0.74
40	I	40.2	1.71	1.06
59	I	17.1	1.66	1.21
59	Al	68.3	1.91	
59	I,Cu	22.8	1.60	1.05
85	I	60.7	1.76	1.07
85	I	25.0	2.28	1.32-1.79
85	I	24.7	2.03	1.07
85	Al	44.0	1.86	
90	I	5.27	1.81	1.03
90	Al	23.0	2.11	
90	Al	29.0	2.83	
90	I,Cu	40.8	1.81	
95	I	3.44	2.27	
95	Al	10.0	1.86	
95	I,Cu	11.8	1.84	

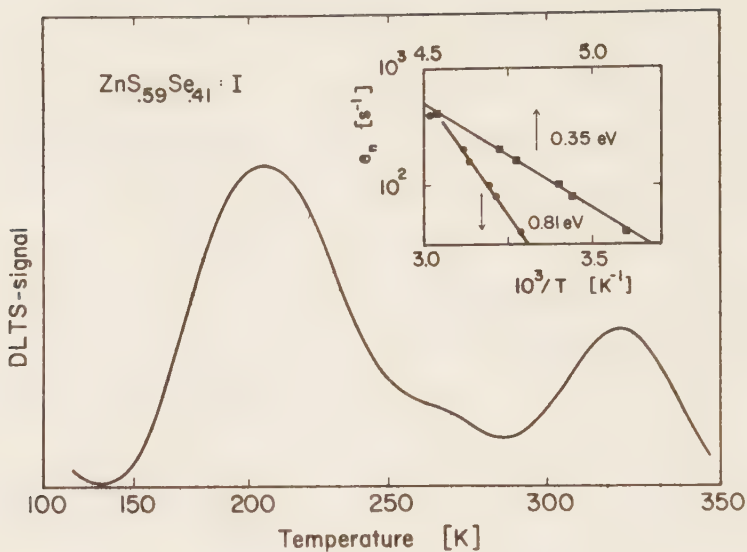


Fig 4. DLTS spectrum. The rate window was 201.2 s⁻¹. The insert shows the Arrhenius plots for the two main peaks.

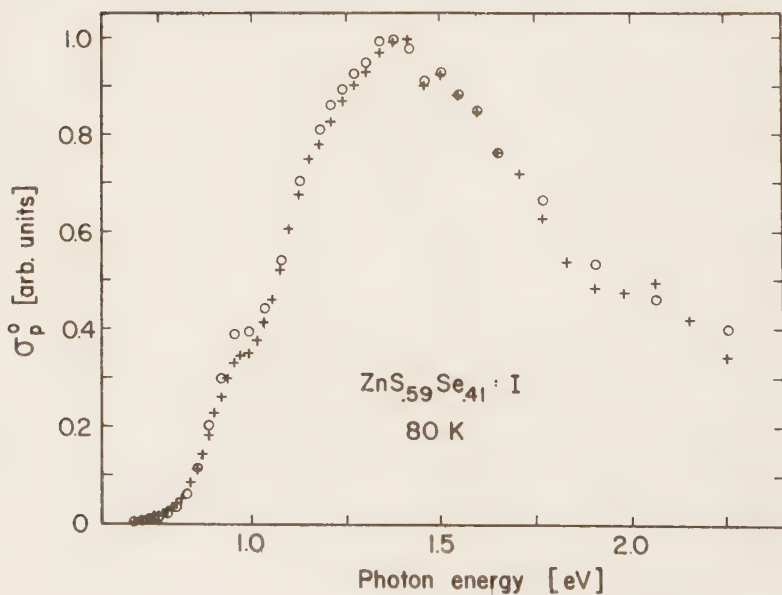


Fig 5. Photoionization cross section of holes σ_p^0 measured by: o) the initial slope and +) the steady state technique ($h\nu_{\text{exc}}=2.90$ eV).

$\epsilon(x) = 9.2 - x/1.14$ (Ref. 2) and is summarized together with values for V_D and η in Table 1 for different compositions. No explanation can be given why n increases when Cu is added to the crystal since previous experiments indicate that Cu doping probably creates a deep acceptor level. It is, however, believed that some of the V_D values are influenced by a surface potential due to interface states. Barrier parameters for metal contacts on $\text{ZnS}_x\text{Se}_{1-x}$ crystals will be discussed elsewhere¹⁸⁾.

The series resistance in our Schottky diodes increases with increasing x and it was therefore not possible to perform any junction measurements at room temperature for compositions larger than $x = 0.95$. It also turned out that difficulties arose in obtaining ohmic contacts on samples with large values of x . Our measurements were therefore restricted to compositions below 96% sulfur. From Hall measurements on the counterparts of our samples¹⁵⁾, it is known that the activation energy of the iodine donor is about 0.01 eV up to $x = 0.6$, but increases to about 0.3 eV at $x = 0.85$. It is expected that the activation energy further increases with increasing values of x . It was therefore not possible to perform any junction measurements below about 200 K with samples in the composition range between 85 and 95% sulfur.

Deep level transient spectroscopy (DLTS)¹⁹⁾ has been used to investigate the presence of electron traps. The experimental arrangement has been described in a previous paper²⁰⁾. The DLTS spectrum of a diode with composition $x = 0.59$ is shown in Fig. 4. From an Arrhenius plot of the thermal emission rate for electrons, e_n^t , activation energies of 0.35 eV and 0.81 eV, respectively, are obtained for the two dominant peaks. The concentration and activation energy of electron traps observed in our

TABLE 2 Electron trap parameters from DLTS spectra for
some $\text{ZnS}_x\text{Se}_{1-x}$ diodes.

x (%S)	Dopant	E_a (eV)	N_{TT} (10^{15} cm^{-3})	
40	I	0.31	3-6	**
59	I	0.35 0.58 0.81	1 1.5	*
59	I, Cu	0.46 0.60	1.3	**,*** *
85	I	0.33 0.52	4	*
85	I	0.37 0.54	<1 5	
90	I	0.38 0.54 0.69	<0.2 2.3	*
95	I	0.52 0.72	<0.1 3	

- * Partly resolved peak
- ** Electric field affected activation energy
- *** Electron occupancy not completely saturated

samples are summarized in Table 2. Because of the very small electron capture cross sections, some of the electron traps could not completely be filled with electrons and, hence, their concentration could not be determined. In some other cases a field dependence of the activation energy was observed implying that different values would be obtained in neutral materials. Some of the peaks could not fully be resolved. For these centers only a very rough estimate of the activation energy is given as indicated in the table. The melting point of the ohmic contact puts a high temperature limit on the DLTS scan implying that electron traps deeper than approximately 1 eV could not be detected. However, using optical methods, no further energy levels have been observed in the samples apart from the deep acceptor levels, which are the object of this investigation.

Since copper is a disturbing impurity in this study of SA centers in $\text{ZnS}_x\text{Se}_{1-x}$ alloys, it is necessary to keep the residual copper concentration as low as possible. As mentioned earlier, extraction in liquid zinc was found to be efficient in ZnSe ¹⁷⁾, and similar treatments were therefore also employed for the purification of the mixed crystals. In spite of this treatment, small concentrations of copper could still be detected by atomic absorption spectroscopy in our samples with $x = 0.85$. The concentration of copper in the as-grown crystals was ca. $7 \cdot 10^{15} \text{ cm}^{-3}$. After extraction, the copper concentration was less than $3 \cdot 10^{15} \text{ cm}^{-3}$ (the detection limit is about 10^{15} cm^{-3}). These values should be compared with the concentration values in samples which were intentionally doped with copper and which contained about $5 \cdot 10^{17} \text{ cm}^{-3}$ copper.

IV Measurements of photoionization cross sections

Absolute values of photoionization cross sections are generally obtained from photocurrent or phot capacitance transient measurements ²¹⁻²⁴). Although photocurrent methods are often a very simple and fast way of measuring spectral distributions of optical emission rates, they are not very useful for measurements on Schottky diodes, since the barrier height normally limits the energy range of the measurements. Only capacitance techniques were therefore used for the study of photoionization cross sections.

The capacitance of a Schottky diode can be written as

$$C(t) = \left[\frac{A^2 q \epsilon \epsilon_0}{2(V_D + V_R)} N_I(t) \right]^{\frac{1}{2}} \quad (2)$$

where A is the area of the barrier, V_D is the diffusion voltage, V_R is the reverse bias and $N_I(t) = N_D - n_T(t)$ is the net concentration of ionized impurities. Here, N_D is the total concentration of shallow donors and ²³⁾

$$n_T(t) = [n_T(0) - n_T(\infty)] \exp[-(e_p + e_n)t] + n_T(\infty) \quad (3)$$

is the time dependence of the concentration of acceptors occupied by electrons where $n_T(0)$ is the initial electron occupancy and $n_T(\infty)$ the equilibrium electron occupancy of the acceptor levels given by ²³⁾

$$n_T(\infty) = \frac{e_p}{e_p + e_n} N_{TT} \quad (4)$$

N_{TT} is the total concentration of acceptor levels and e_n and e_p are the emission rates for electrons and holes. It should be noted that the emission

rate $e_{n,p} = e_{n,p}^o + e_{n,p}^t$ is the sum of the optical and thermal emission rates. The optical emission rate e^o is correlated to the photoionization cross section σ^o by the relation $e^o = \sigma^o \cdot \phi$ where ϕ is the photon flux used for measuring e^o . In the case of exponential transients the initial slope of the capacitance transient is proportional to

$$\left. \frac{dC}{dt} \right|_{t=0} \propto \left[n_T(0) - \frac{e_p}{e_p + e_n} N_{TT} \right] (e_p + e_n) \quad (5)$$

Hence, for $n_T(0) = N_{TT}$ the slope is proportional to e_n , whereas for $n_T(0) = 0$ the slope is proportional to e_p . Since our capacitance transients were not simple exponential ones, it was not certain whether or not the initial slope technique could be used in our case. To check this, the spectral distribution of the hole emission rate was measured in some of our samples using the steady-state capacitance technique²⁵⁾. This technique implies that the occupancy of the energy level concerned is nearly kept constant by illuminating the sample with an additional light source of high photon flux ϕ_s when measuring the emission rate with a light source of variable energy $h\nu$ and much smaller photon flux ϕ . Using Eqs. 2 and 4 the small change in capacitance caused by the probe light can easily be calculated by differentiating Equ. 2 with respect to the emission rates giving

$$\Delta C = \frac{A^2 q \epsilon \epsilon_0}{4C(V_D + V_R)} N_{TT} \tau_s \left[b e_n - (1-b) e_p \right] \quad (6)$$

Here $b = e_{ps}^o / (e_{ps}^o + e_{ns}^o)$ is the electron occupancy of the acceptor levels owing to the additional light source of photon flux ϕ_s and τ_s is the inverse sum of the emission rates ($e_{ns}^o + e_{ps}^o$). Since the photon energy $h\nu_s$ of the additional light source is constant, both b and τ_s are constants. By choosing $h\nu_s$ such that $E_C - E_T < h\nu_s < E_g$ and, hence, $0 < b < 1$ the

spectral distribution of the hole emission rate can readily be measured for all photon energies for which $e_p^0 \gg e_n^0 b / (1-b)$. A typical spectrum obtained with this technique is shown in Fig. 5 for a sample with 59% sulfur. For comparison, a spectrum measured with the initial slope technique is also shown. The good agreement of the two spectra clearly demonstrates the usefulness of the initial slope technique even for non-exponential transients. Since the steady-state technique is faster and less influenced by the capture of electrons from the free carrier tail ²⁶⁾, this technique was used whenever possible. In the few cases the steady-state technique was not applicable, for example due to the instability of the initial electron occupancy, the initial slope method was employed.

V Experimental Results

A PHOTOIONIZATION CROSS SECTION SPECTRA

One of the reasons for the investigation of photoionization cross sections was to improve our understanding of the electronic properties of the selfactivated center in II - VI compounds. Optical emission spectra have proven to be very useful in this context. Fig. 6 shows the photoionization cross section spectra of holes obtained in samples of different composition not intentionally doped with deep impurities. All spectra consist of a main peak at higher energies, and a smaller peak or bump at lower energies. Similar spectra have been obtained in ZnS by Koda and Shionoya ⁶⁾ from optical quenching of the selfactivated blue luminescence. A two-band quenching spectrum was also observed in ZnS by Watkins ⁷⁾ when measuring the optical bleaching rate of the ESR signal originating from the A-center. The low energy peak in this investigation lies at 0.95 eV, which is very

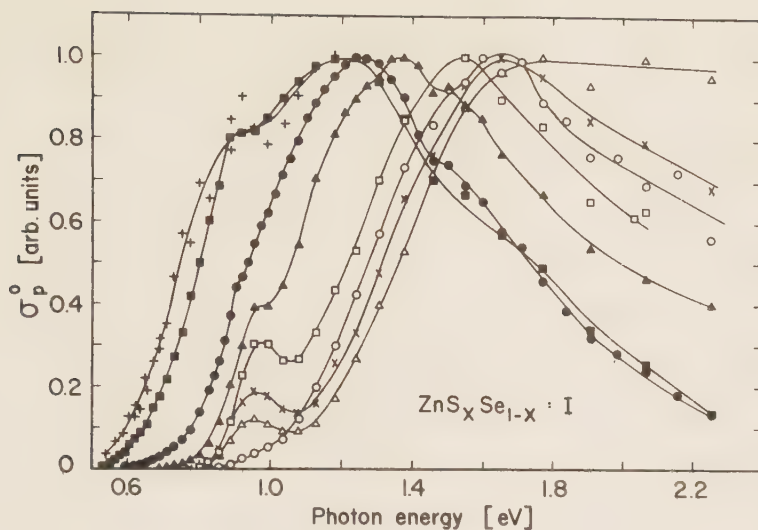


Fig 6. Spectra of the optical hole emission cross section as a function of composition. The symbols are explained in Fig 7. Two spectra are shown for the sample with 59% S differing in the photon energy of the excitation light: $h\nu_{\text{exc}} = \blacksquare$) 2.43 eV, $\blacktriangle$) 2.90 eV.

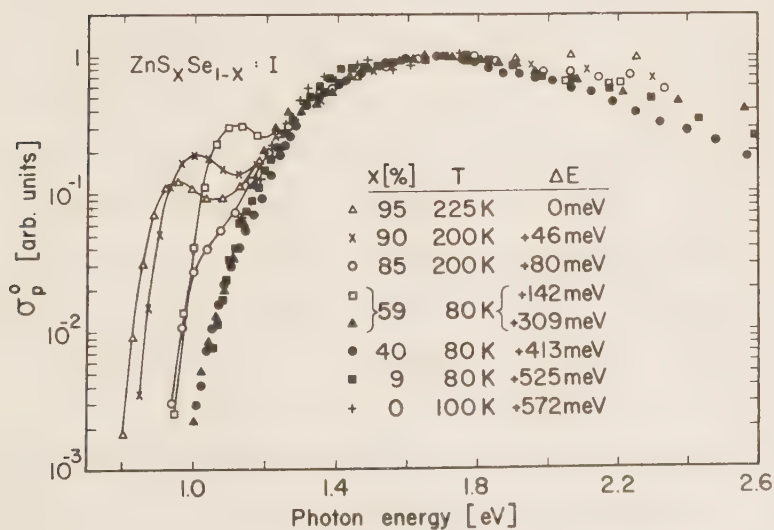


Fig 7. The spectra of σ_p^0 from Fig 6 shifted in energy to make the high energy parts to coincide.

close to the position of the peak observed in our samples with sulfur concentrations larger than 55%, whereas the threshold for the high energy peak is shifted somewhat to lower energies compared with our results. Similar properties are valid for the spectrum of the 3S center in $\text{ZnS}_{0.98}\text{Se}_{0.02}$ studied by Schneider et al using optical quenching of the ESR signal ¹³⁾. In their crystal, three A-centers were observed. The spectrum of one of them which was attributed to the 1Se center, shows a very close resemblance to the spectrum obtained in our sample with 95% sulfur if the low energy peak is neglected. A peak at 0.95 eV was also observed in ZnS when measuring optical quenching of photoconductivity ²⁷⁾, although the threshold for the high energy peak lies at still higher energies than in our sulfur rich samples.

The spectra of Fig. 6 are replotted in Fig. 7, but shifted to higher energies until the threshold of the main band coincides with the spectrum obtained in the sample with $x = 0.95$. Owing to the good agreement thus obtained for the main band in samples of different compositions, it is reasonable to explain this part of the spectrum as being caused by hole excitation from the A-center directly into the valence band. The energy shift of the spectra corresponds then to the relative change of the binding energy with composition for the A-center. The absolute values of the binding energy were estimated by taking the $x = 0.09$ spectrum as reference (Table 4) since the low energy range of this spectrum appears to be undisturbed by further peaks.

Several measurements were performed to find out whether the low energy peak in our spectra is part of the total spectrum and, hence, originates from an excited state or resonance state, or is caused by a different

defect. All results obtained seem to indicate that all centers are completely filled with electrons when illuminating the samples with a photon energy corresponding to the low energy peak. However, for several reasons this does not necessarily imply that the low energy peak is caused by the same center. Since the two bands are rather broad, overlap cannot be excluded for the photon energies used in the experiment. Furthermore, owing to the non-exponential transients, it is difficult to decide when steady-state is reached. Another disturbing factor is the observation that electrons probably are excited thermally into the acceptor levels, although the binding energy should be large enough to prevent such a thermal excitation. Similar properties were observed by Schneider et al ¹³⁾ in their crystals. Their assumption that the effect is due to the capture of electrons which have been released from other traps by stimulated thermal emission, can probably be ruled out in our case, since such electrons would quickly be swept out of the space charge region by the electric field. Finally, owing to the limited temperature range in which our samples could be measured, we were unable to see any thermal activation, which would be expected if the low energy peak results from a photothermal process via an excited hole state close to the valence band. The only temperature dependence observed was some broadening of the bands.

The shape of the low energy peak is very close to a gaussian distribution. By fitting such a distribution to the measuring points and then subtracting it from the experimental data, in order to obtain a better defined threshold for the main band, it turned out that, for all samples in the sulfur rich composition range, a value of 0.95 eV was obtained for the peak energy independent of the composition. For the selenium rich samples, the peak appears to merge into the main band, which makes any further analysis

somewhat difficult. Nevertheless a closer inspection of the data gives reason to believe that another peak is showing up at about 0.9 eV.

There are several possible reasons why the transients measured are not exponential. Inhomogeneity of the light intensity could be one reason, but using a semi-transparent gold contact did not improve the transients. Yet there may exist microscopic sources of absorption or reflection. Considerable compensation of shallow donors could be another reason, but constant capacitance measurements did not result in simple exponential transients. Compensation is expected to cause disturbances of the initial part of the transient and should not give rise to slow tails, as observed. The same argument holds for effects due to free carrier tails²⁶⁾. Contributions from several centers with different emission rates is another reason for non-exponential decays. The expected dependence of the transient waveform on photon energy was, however, not observed. In addition, the time dependence of the decay for the dominating centers in seleniumrich and sulferrich samples were not very different, and it is therefore unlikely that the very slow tails are due only to the presence of different SA centers. Electrical field barrier lowering, energy level and band broadening, all give rise to distributions in activation energies, which lead to nonexponential decays. Furthermore, recapture of excited holes would complicate the reaction kinetics severely. The probability of such a process depends on the hole transit time, which in turn depends on the transition region width. However, under forward bias conditions, similar nonexponential decays were obtained. Energy transfer processes between closely spaced energy states are further reasons for nonexponential decays in mixed crystals. Since nonexponential decays were also observed in pure ZnSe, their origin cannot be due only to mixing disorder.

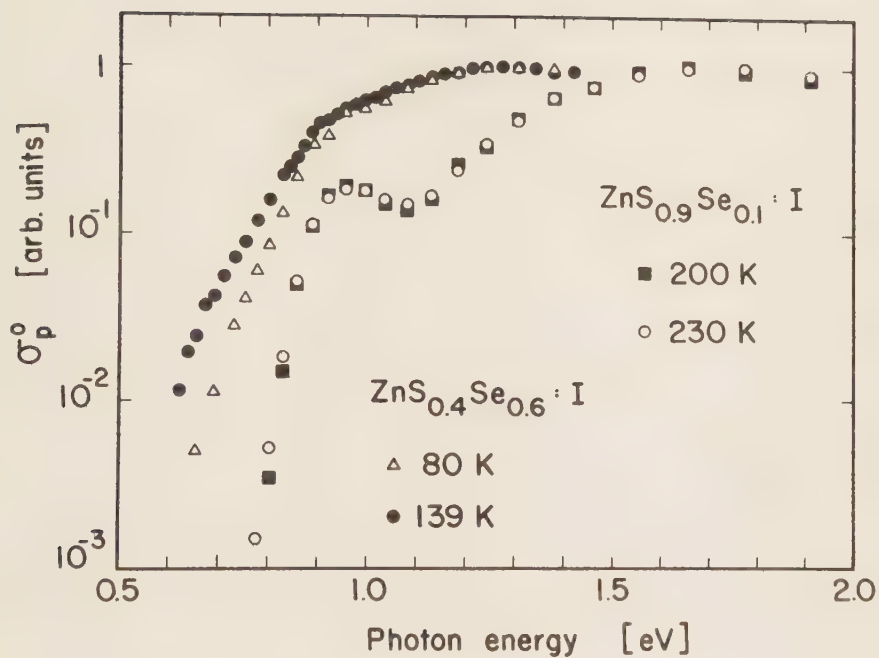


Fig 8. Temperature dependence of σ_p^0 for two samples with different compositions.

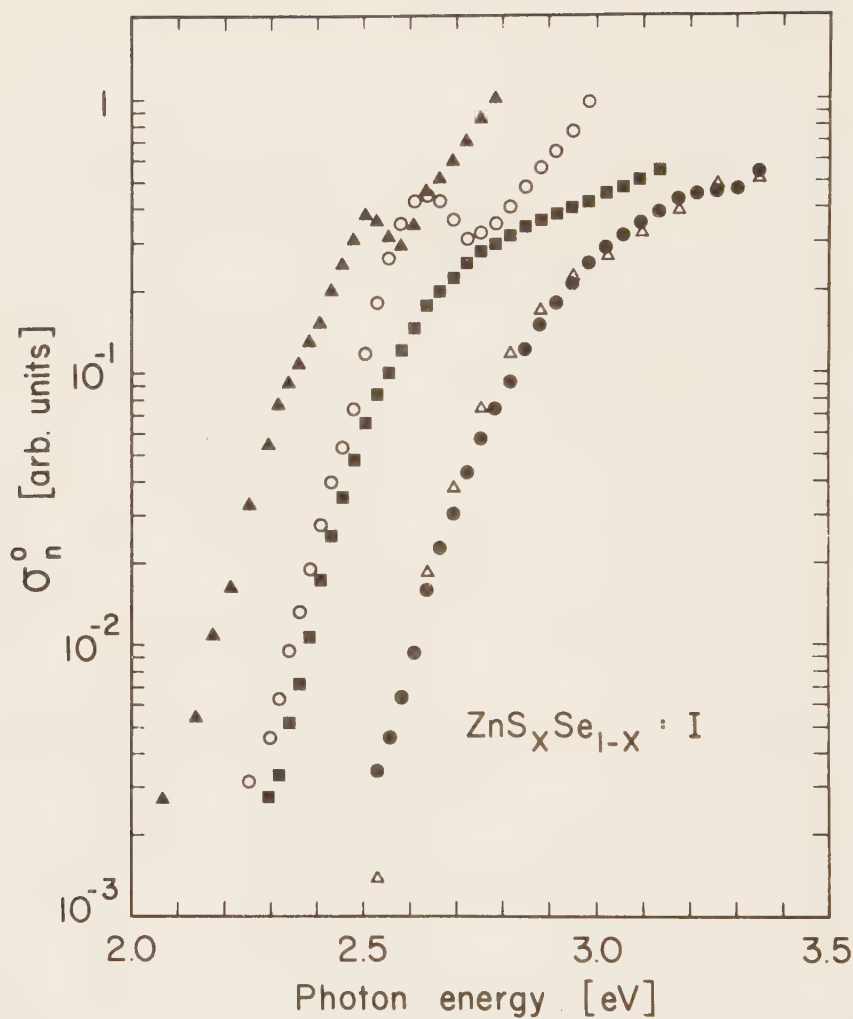


Fig 9. Photoionization cross section spectra of electrons σ_n^0 at different compositions. The symbols are explained in Fig 10.

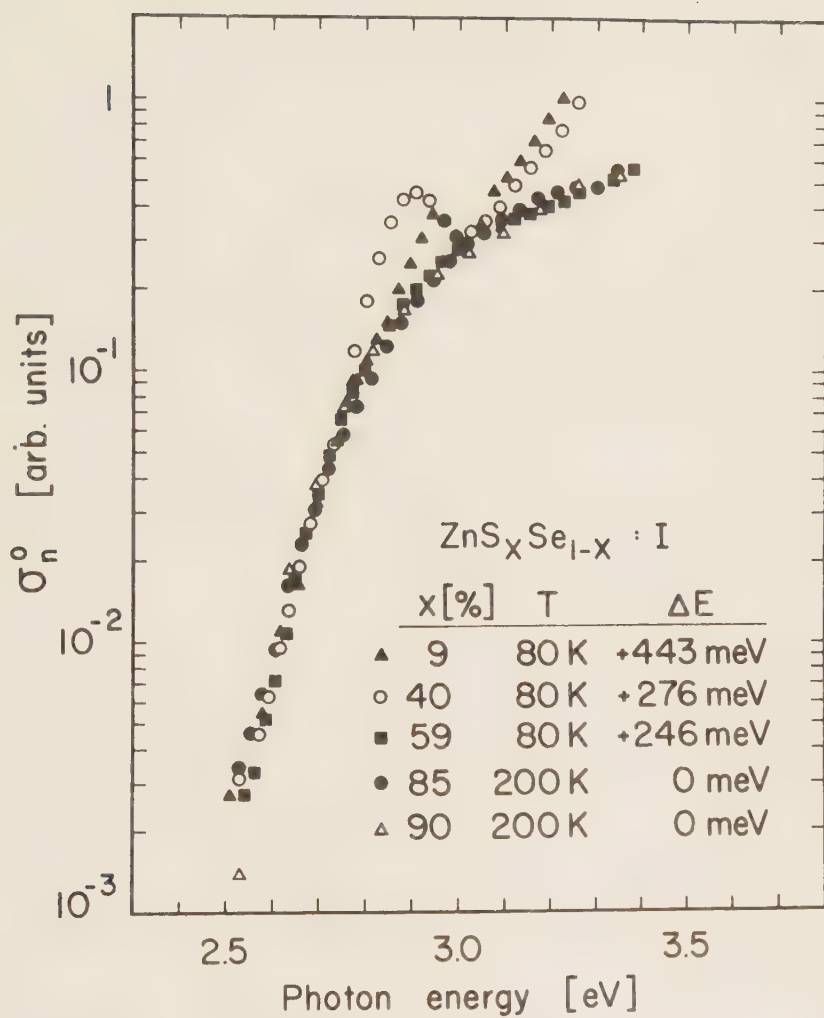


Fig 10. The spectra of σ_n^0 from Fig 9 shifted in energy position to obtain coincidence of the low energy edges.

The temperature dependence of σ_p^0 was measured in most of our samples. The temperature broadening observed was very small in the sulfur-rich samples compared with the pronounced broadening in samples up to $x \approx 0.6$ (Fig. 8).

Photoionization cross sections for the excitation of electrons into the conduction band are shown in Fig. 9. Good agreement is observed for the shape of these spectra on the low energy side of the peak by shifting the spectra along the energy scale (Fig. 10). After estimating the threshold energy for the 90% sulfur composition, which had the simplest spectrum, the threshold energies of all other compositions are given by their relative energy shift obtained from Fig. 10. The threshold energies, E_n , determined in this way are summarized in Table 4.

Although the sulfur-rich samples did not show any structure in the spectrum of σ_n^0 , it is interesting to note that the selenium-rich samples exhibited a clearly resolved peak followed by a much sharper rise in the spectrum than for the sulfur-rich samples. Furthermore, the maximum of this peak shifts to higher energies with increasing selenium concentration, in contrast to the 0.95 eV peak in the σ_p^0 spectra which always occurs at the same energy.

Before fabrication of the Schottky barriers, the crystals were cleaved. The cleaved surface of one piece of the crystal was used for the diode fabrication and the surface of the other piece was employed for photoluminescence measurements. The emission spectra obtained are shown in Fig. 11. They are in good agreement with measurements on powder samples performed by Lehmann³⁾. It is readily seen that at least two separate

emission bands can be resolved in samples with a sulfur concentration larger than 59%, the two bands can be separated by using different photon energies for the excitation of these samples ¹⁵⁾. Although varying the excitation energy did not result in any structure for samples with sulfur concentrations of 20, 40 and 59% the peak nevertheless shifted about 0.1 eV ¹⁵⁾.

In order to correlate the luminescence data with those obtained from photocapacitance measurements, an attempt was made to estimate the energy position of the final state involved in the luminescence process. Assuming that only phonon emission has to be considered, the final state energy can be estimated from the high energy threshold of the emission band. These thresholds are summarized together with the peak energies of the photoluminescence in Table 4. Since the luminescence is believed to be a DA pair recombination ⁸⁻⁹⁾, the values for thresholds have to be corrected for the donor binding energy in order to be comparable with the energy position of the final states. Since no further information on the donors involved was available, the uncorrected values are given in Table 4.

B DEPENDENCE OF σ_p^0 ON EXCITATION ENERGY

In order to establish whether the four-center model of Fonger ¹²⁾ is appropriate for the description of the SA-center in $\text{ZnS}_x\text{Se}_{1-x}$ alloys, the spectral distribution of optical emission rates was measured using different photon energies for excitation. At least two of the four centers, namely the 3S- and 3Se-center, must exist since they are present in ZnS and ZnSe, respectively. It is also quite probable that the 1Se center exists thanks to the data obtained by ODMR in 95,5% sulfur alloys ¹⁴⁾ and by ESR together

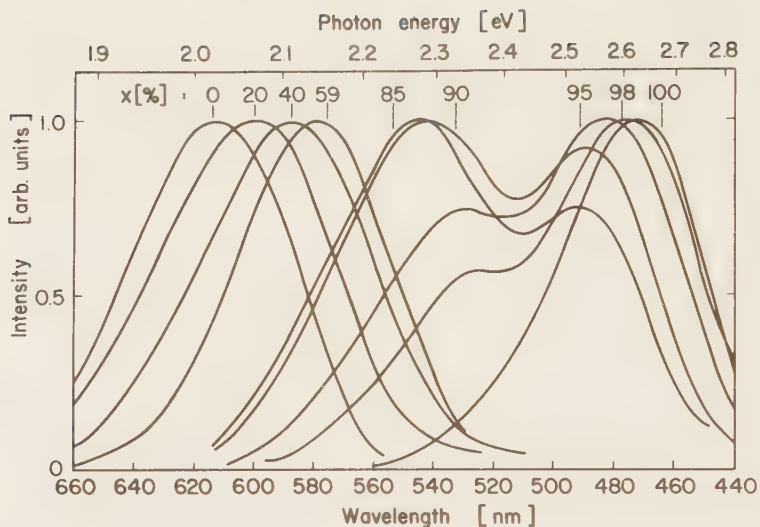


Fig 11. Luminescence spectra of $\text{ZnS}_x\text{Se}_{1-x}:\text{I}$ crystals at 27K. The photon energy of the excitation light was 3.4 eV.

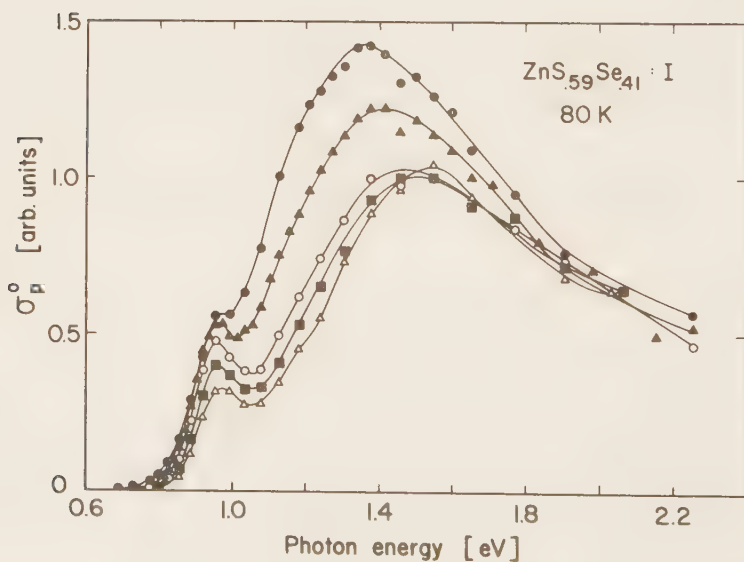


Fig 12. σ_p^0 in the 59% S sample for various excitation conditions: $h\nu_{\text{exc}} = \Delta$) 2.43 eV, $\blacksquare$) 2.48 eV, $\circ$) 2.56 eV, $\blacktriangle$) 2.70 eV, $\bullet$) 2.90 eV.

with the 2Se center in 98% sulfur samples¹³⁾. A further hint is obtained from our photoluminescence data in sulfur rich alloys.

A reproducible influence of the excitation energy on the spectrum of σ_p^0 was only observed in crystals of composition $x = 0.59$ (Fig. 12). With increasing excitation energy the main peak gradually shifts 0.17 eV to lower energies. We were unable to decide whether this shift is caused by a single energy level closer to the valence band or by several close lying energy levels. It should be noted that the low energy peak is completely unaffected by the change in excitation energy and obviously does not gain any strength from the growing signal of the main peak. Similar measurements in $\text{ZnS}_{0.4}\text{Se}_{0.6}$ and $\text{ZnS}_{0.85}\text{Se}_{0.15}$ are shown in Fig. 13. No reproducible changes are observed in these materials as in all other samples.

Specific detailed measurements were performed on the 85% sulfur samples, since we expected to see the two centers causing the two peaks in photoluminescence. Although a spectrum of a second energy level could not be measured, there is nevertheless reason to believe that a second level lying closer to the valence band may exist. As soon as the photon energy of excitation becomes larger than $E_C - E_T$ where E_T is the energy position of the center, the capacitance increased rapidly owing to the decrease in the electron occupancy of the center. When the light source is turned off, the capacitance decreases because of the electron capture in the edge region of the space charge region. For excitation energies much larger than $E_C - E_T$ the capacitance signal increases considerably. After the light source is removed, a capacitance value is obtained similar to that for smaller excitation energies. The decay is therefore much larger than can be

explained by electron capture alone. It is therefore believed that the decay is due to thermal emission of holes from another center which is closer to the valence band and which may be responsible for the high energy peak in photoluminescence. Such a center should lie about 0.3 eV closer to the valence band. Since our measurements could only be performed at temperatures higher than 200 K, it is reasonable that under these conditions a spectrum of σ_p^O for the shallower center cannot be obtained because of the thermal release of holes.

C DIFFERENT DOPING

In order to investigate the influence of different donor levels on the properties of the SA-center, a preliminary study was performed by doping the $\text{ZnS}_x\text{Se}_{1-x}$ alloys with aluminum. Since the crystals were synthesized by using the iodine vapor transport method, there is probably a residual concentration of iodine in the samples. It is, however, expected that aluminum forms the dominant donor level. There is reason to believe that the aluminum A center is more complicated than the halogen A center. However, owing to the preliminary character of the study, only the experimental results are presented without any detailed discussion.

Schottky diodes of high quality could be fabricated only in samples with 85 and 90% sulfur. The spectra of σ_p^O obtained in these samples are shown in Fig. 14. The low energy peak was less pronounced in Al doped samples than in I doped samples but was clearly present even in crystals of different compositions. The main peak was obviously shifted to lower energies. The shift can be estimated by extrapolating the low energy range of the spectra giving a value of about 28 meV (Fig. 14).

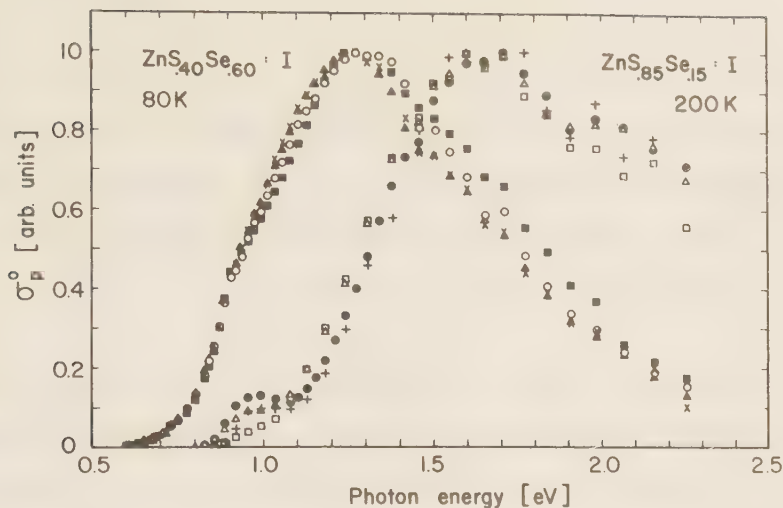


Fig 13. σ_p^0 for different excitation light photon energies in $\text{ZnS}_{.40}\text{Se}_{.60}\text{I}$, $h\nu_{\text{exc}} = \blacksquare$) 2.43 eV, $\circ$) 2.53 eV, $\blacktriangle$) 2.58 eV, $\times$) 2.64 eV, and in $\text{ZnS}_{.85}\text{Se}_{.15}\text{I}$, $h\nu_{\text{exc}} = +$) 2.58 eV, $\bullet$) 2.70 eV, Δ) 2.95 eV, $\square$) 3.18 eV.

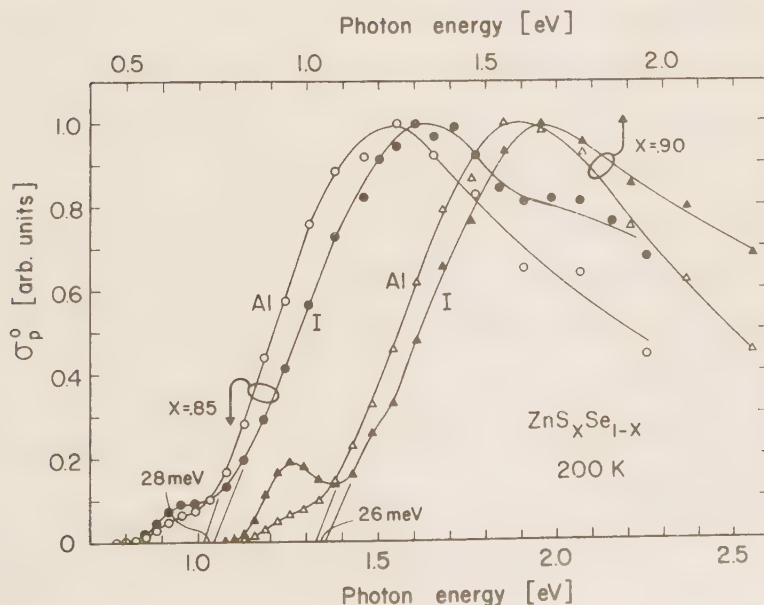


Fig 14. Comparison of σ_p^0 spectra measured in Al- and I-doped crystals. The two pairs of spectra for different compositions are shifted 0.3 eV for clarity.

In order to confirm these data, the spectrum of σ_n^0 was measured in the 85% sulfur sample (Fig. 15). The relative energy position of the spectrum was obtained by shifting the spectrum of the I doped sample to higher energies. Best agreement was observed for a shift of 28 meV thus confirming our data obtained for the hole transition.

If these results imply that the Al-A-center lies 28 meV closer to the valence band, a corresponding shift should be observed in photoluminescence. Photoluminescence spectra were therefore studied in aluminum-doped samples of different composition. These spectra were not much different from the results obtained in I doped samples except that the peaks were shifted to lower energies by 10 - 30 meV. Such shifts both to higher and lower energies have been observed previously ^{3, 28)}. Our photoluminescence data may imply that the Al-A-center has a binding energy larger than the I-A-center, in spite of the results obtained from our photoionization cross section measurements. This obvious discrepancy of the data may have to do with the nature of the recombination processes giving rise to the photoluminescence emission, which has been suggested to be caused by DA pair recombination ⁸⁻⁹⁾. The initial states involved are, however, not identified, and it is therefore not clear whether or not they are identical with the dominant shallow donors. In fact, the binding energy of the dominant iodine donor varies substantially when the sulfur content increases from 59% to 85% ¹⁵⁾, while no remarkable changes in the photoluminescence data are observed. The situation may be further complicated owing to the high aluminum doping, which may give rise to shallow donor interaction.

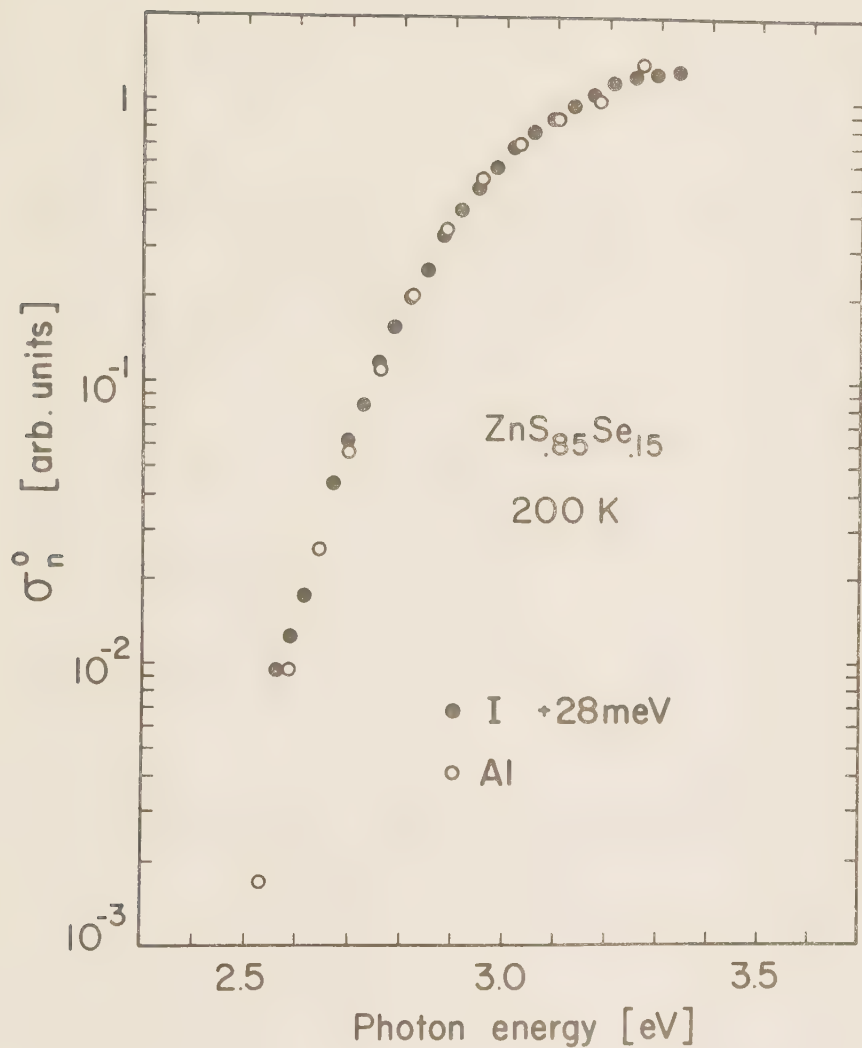


Fig 15. σ_n^o spectra for Al- and I-doped crystals. The spectrum of the I-doped sample is shifted to obtain the relative threshold energy.

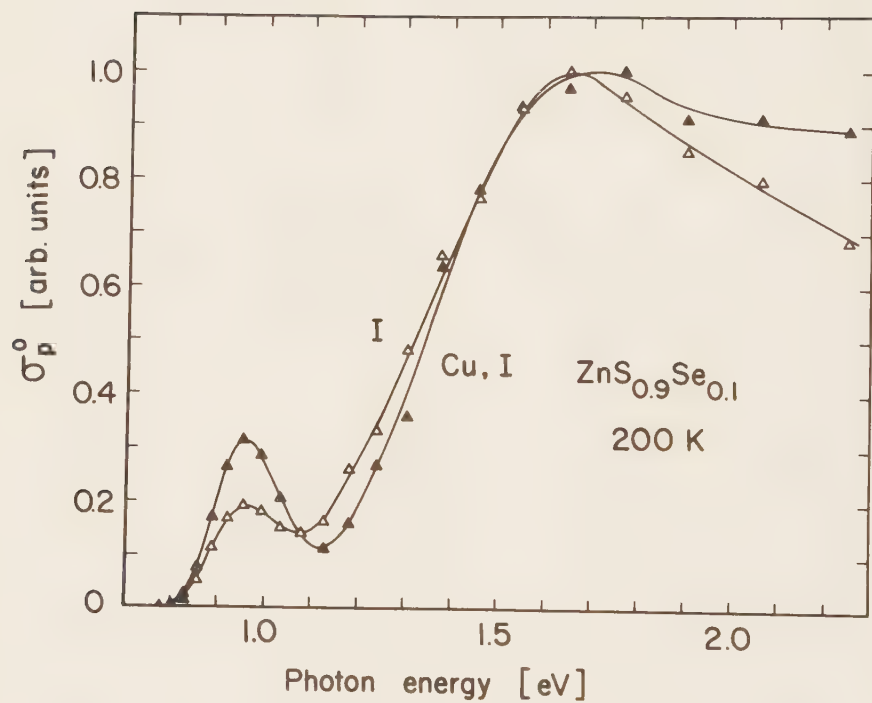


Fig 16. Comparison of σ_p^0 measured in two I-doped samples, one of them additionally doped with Cu.

A few measurements were also performed on copper-doped $\text{ZnS}_{0.9}\text{Se}_{0.1}$. The spectrum of σ_p^0 is shown in Fig. 16. The similarity of the spectrum to the one obtained in samples not intentionally doped with copper is striking. It was therefore carefully checked that the copper concentration in the copper doped samples was several orders of magnitude larger than in the ones not deliberately doped (Section III) and that the photocapacitance signals in both the undoped and the copper doped samples were of the same order of magnitude. Furthermore, the photoluminescence decay properties of these samples were in agreement with what one would expect for the copper green and SA green emission. It can therefore not be excluded that the Cu related center and the I-A-center may have comparable binding energies. It should be noted that the low energy peak in the copper-doped alloy is very pronounced and much stronger than in samples not intentionally doped with copper.

VI Discussion

The similarity of the σ_p^0 spectra obtained in not intentionally-doped and copper doped samples (Fig. 16) raises the question whether the center investigated by us really is the SA center or rather the copper related acceptor level studied, for example, by junction space charge techniques in ZnSe:Cu ²⁹⁾ and discussed in several previous papers. Although residual copper concentrations cannot be excluded in our samples (and in fact have been detected in some of the samples), it is quite clear that the copper concentration in the not deliberately doped samples was several orders of magnitude smaller than in the copper doped samples. Furthermore the luminescence decay properties were proven to be different in these samples and could readily be correlated with those properties known from

other investigations ⁴⁾ on the SA and copper emission. It is also known from ODMR measurements that the SA center and a copper related center may have similar energy positions in ZnSe ³⁰⁾. There is therefore reason to believe that the center investigated by us is indeed the SA center.

This interpretation is supported by the results shown in Figs. 14 and 15. Aluminum doping obviously has some influence on the σ_p^0 and σ_n^0 spectra, indicating that the center may be a complex involving a different donor level than the Cu-center.

Although several energy levels were found in the upper half of the band gap in our samples, we were unable to detect further energy levels in the lower half of the band gap except the SA center. Seven different electron traps were identified by Besomi and Wessels ³¹⁾ in ZnSe (Table 3). One of these traps, with an activation energy of 0.36 eV, has very similar properties compared with the dominant electron trap studied by Shrikawa and Kukimoto ³²⁾ in the $\text{ZnS}_x\text{Se}_{1-x}$ alloys. These authors found that the activation energy of this trap (0.33 eV) was independent of composition. They also detected a second, slightly deeper trap at 0.36 eV below the conduction band ³³⁾. Kosai ³⁴⁾ recently observed four electron traps in ZnSe. The activation energy of the trap at about 0.35 eV, however, varied in different samples, and so did the capture cross section. An energy level was found at about 0.35 eV below the conduction band in most of our samples (Table 2). We therefore assume that this level is identical with the one observed by other authors and is supposed to be caused by an anion vacancy ³²⁾ or at least a family of anion vacancy related complexes ³⁴⁾.

TABLE 3 Publish activation energies of electron traps in $\text{ZnS}_x\text{Se}_{1-x}$ crystals obtained from DLTS. The activation energies are calculated directly from $\log e_n - T^{-1}$ plots. The traps of Ref. 31 were not all found in the same sample.

$\text{ZnS}_x\text{Se}_{1-x}$		ZnSe			
ref 32		E_a (eV)			
x(%S)	E_a (eV)	ref 31	ref 33	ref 34	
0	0.32	0.26		0.19	
12	0.32	0.36	0.33	0.43	0.33 0.36
17	0.33	0.39	0.36	0.70 0.71	
44	0.33	0.47			
66	0.33	0.60			
		0.78			
		0.94			

A low energy peak at 0.85 eV in the σ_p^0 spectrum of ZnSe:Cu and a corresponding one at 0.91 eV in ZnS:Cu have previously been reported and discussed in detail ^{29,35)}. The situation in the not deliberately-doped samples seems to be similar, and may be explained by either excited hole state or resonance states, since no drastic change in the density of states ³⁶⁾ occurs at these energies. It is interesting to note that with increasing sulfur content the low energy peak in the σ_p^0 spectrum disappears in samples in which the low energy peak started to show up in the σ_n^0 spectrum. The data presented in Fig. 9 clearly show that the peak shifts to higher energies with increasing sulfur content. Structures in the σ_n^0 spectrum have previously been reported for ZnSe:Cu ²⁹⁾. Low energy peaks have not only been observed in ionic crystals such as II-VI compounds, but also in silicon. Humphreys ³⁷⁾ obtained spectra very similar to ours by measuring photoconductivity in electron (2 MeV) irradiated boron doped silicon without any distribution.

The threshold energies obtained from different measurements for the only deep center observed in the lower half of the band gap are summarized in Table 4 and Fig. 17, together with the values for the band gap energies E_g ³⁸⁻⁴⁰⁾. It is quite obvious that the sum of the threshold energies for corresponding hole and electron transitions do not add up to the band gap energy in any of the compositions. One reason why the sums are smaller than the band gap energy may be explained by the absence of theoretical models describing the spectral distribution of photoionization cross sections. This makes any determination of threshold energies somewhat arbitrary. In addition, phonon broadening may be another contributory factor to the large discrepancy between the sums of the threshold energies and the band gap energy. Nevertheless, using our values for the threshold energies, some trends may be visualized.

TABLE 4. Energy levels obtained from optical measurements.

E_p and E_n are the threshold energies of σ_p^0 and σ_n^0 , respectively. E_l is the position of the luminescence peak and E_r is the threshold energy estimated from luminescence data. E_l and E_r are determined at 27 K while all other energy levels are obtained at the temperature given in the table.

x (%S)	T (K)	E_g (eV)	E_p (eV)	$E_g - E_p$ (eV)	E_n (eV)	E_r (eV)	E_l (eV)	$E_g - E_p - E_n$ (eV)
0	100	2.80	0.45	2.38		2.19	2.02	
9	80	2.87	0.50	2.41	2.08			0.29
20	80	2.95				2.27	2.07	
40	80	3.12	0.61	2.54	2.24	2.32	2.10	0.27
59	80	3.31	0.72 0.88	2.63 2.46	2.27	2.35	2.14	0.32 0.16
85	200	3.55	0.95	2.64	2.52	2.47 2.73	2.27 2.52	0.08
90	200	2.62	0.98	2.68	2.52	2.49 2.75	2.28 2.53	0.12
95	225	3.68	1.03	2.69		2.56 2.82	2.34 2.56	
98						2.60 2.85	2.36 2.60	
100						2.85	2.62	

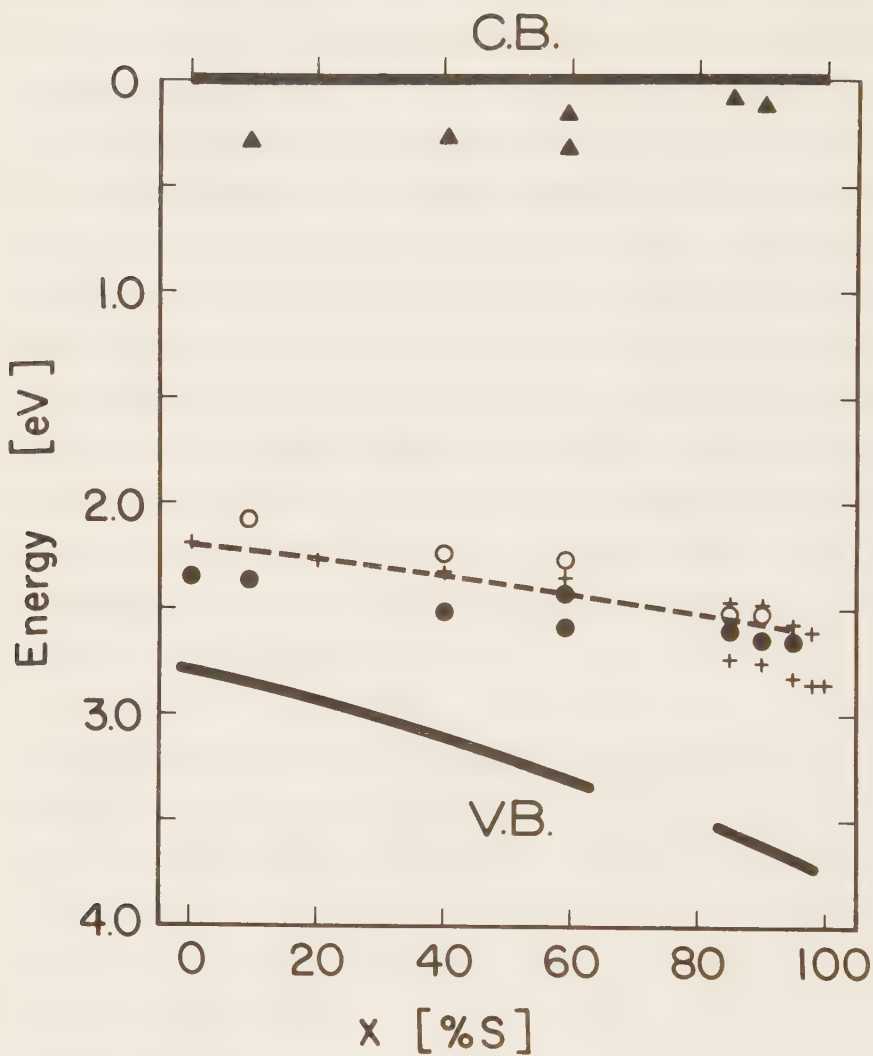


Fig 17. Energy level scheme of $\text{ZnS}_x\text{Se}_{1-x}:\text{I}$ mixed crystals from optical experiments. The energy levels are taken from Table 4. $\bullet$) $E_g - E_p$, $\circ$) E_n and $\blacktriangle$) $E_g - E_p - E_n$ are given at the temperature written in Table 4 for each composition while $+$) E_p is determined at 27K.

Furthermore, since the luminescence data were taken at 27 K, whereas all photocapacitance data were obtained at 80 K or higher temperatures, one would expect that as a result of the smaller phonon broadening, the threshold energies deduced from the luminescence spectra would result in energy positions for the center which lie between those obtained from the σ_p^0 and σ_n^0 spectra. This is indeed observed for compositions smaller than $x = 0.8$. Considering that the energy positions obtained from the luminescence data are not corrected for any donor binding energy, and that the dominant donor is very shallow for compositions up to $x = 0.59$, whereas the binding energy of the donor increases considerably for $x \geq 0.85$, it is quite conceivable that the energy positions obtained from the luminescence data should lie closer to the valence band for $x \geq 0.85$ if the photoluminescence is caused by a DA recombination process. This implies that the true binding energy of the SA center probably is close to the dashed line indicated in Fig. 17.

Since our spectra do not show any refined structure, we were unable to confirm the four-center model. On the basis of the data published in literature, there is, however, strong reason to believe that four different SA centers may exist. Our measuring techniques are therefore not able to resolve the optical properties of these centers, probably because of relatively broad bands with only small differences in threshold energies. Spin dependent effects may give better results. If the four-center model is valid, the measuring techniques used in this paper will give only the overall spectra of all energy levels involved in the center, and the signal will be weighted by the relative concentrations (Fig. 2).

A closer inspection of Fig. 17 shows that at least two interpretations of our results are possible. If the SA center mainly follows the valence band, one is inclined to believe that the 3Se-center has a smaller binding energy than the 3S-center, which is somewhat surprising, considering that S is more electronegative than Se. In fact, Block and Cox¹⁴⁾ identified the 3S- and 1Se-center in a 95.5% S sample and found that the 1Se-center obviously is deeper than the 3S-center if the initial states of the recombination processes have similar energy positions in both cases. If it is therefore assumed that the Se-centers create the deeper acceptor levels, then it has to be concluded that the SA center is mainly pinned to the conduction band. As mentioned earlier, different experiments have to be performed to obtain further information on the electronic properties of the SA center in the $\text{ZnS}_x\text{Se}_{1-x}$ alloys.

ACKNOWLEDGEMENT

The authors would like to thank G. Müller for valuable discussions and critically reading the manuscript. They also gratefully acknowledge the financial support of the Swedish Natural Science Research Council and the Swedish Board for Technical Development.

REFERENCES

- 1 H. Hartmann, R. Mach and B. Selle in Current Topics in Material Science, Vol. 9, North Holland Publ. Co., Amsterdam/New York (1982).
- 2 R. K. Watts, Point Defects In Crystals, Chap. 9, Wiley-Interscience (1977).
- 3 W. Lehmann, J. Electrochem. Soc. 114, 83 (1967).

- 4 K. Era, S. Shionoya and Y. Washizawa, J. Phys. Chem. Sol. 29, 1827 and 1843 (1968).
- 5 Y. Canér, A. Scharmann and D. Schwabe, J. Lum. 22, 79 (1980).
- 6 T. Koda and S. Shionova, Phys. Rev. 136, A541 (1964).
- 7 G. D. Watkins, Solid State Comm. 12, 589 (1973).
- 8 J. E. Nicholls, J. J. Davies, B. C. Cavenett and D.J. Dustan, J. Phys. C. 12, 361 (1979).
- 9 D. J. Dunstan, J. E. Nicholls, B. C. Cavenett and J. J. Davies, J. Phys. C. 13, 6409 (1980).
- 10 J. Schneider, II-VI Semiconducting Compounds, p 40 (Edited by D. G. Thomas), Benjamin, New York (1967).
- 11 B. Dischler, A. Räuber and J. Schneider, Phys. Stat. Sol. 6, 507 (1964).
- 12 W. H. Fonger, Phys. Rev. 137, A1038 (1965).
- 13 J. Schneider, B. Dischler and A. Räuber, J. Phys. Chem. Sol. 31, 337 (1970).
- 14 D. Block and R. T. Cox, J. Lum. 24/25, 167 (1981).
- 15 R. Mach, P. Flögel, L. G. Suslina, A. G. Areshkin, J. Maege and G. Voigt, Phys. Stat. Sol. (b) 109, 607 (1982).
- 16 M. de Murcia, D. Block, D. Etienne and J. P. Fillard, J. Phys. Chem. Sol. 41, 1247 (1980).
- 17 H. G. Grimmeiss, C. Ovrén, W. Ludwig and R. Mach, J. Appl. Phys. 48, 5122 (1978).
- 18 R. Mach, unpublished.
- 19 D. V. Lang, J. Appl. Phys. 45, 3014 and 3023 (1974).
- 20 L. Jansson, V. Kumar, L.-Å. Ledebø and K. Nideborn, J. Phys. E. 14, 464 (1981).
- 21 H. G. Grimmeiss, Ann. Rev. Mater. Sci. 7, 341 (1977).

- 22 G. L. Miller, D. V. Lang and L. C. Kimerling, *Ann. Rev. Mater. Sci.* 7, 377 (1977).
- 23 H. G. Grimmeiss and C. Ovrén, *J. Phys. E.* 14, 1032 (1981).
- 24 H. G. Grimmeiss, *J. Cryst. Growth* 59, (1982).
- 25 H. G. Grimmeiss and N. Kullendorff, *J. Appl. Phys.* 51, 5852 (1980).
- 26 H. G. Grimmeiss, L.-Å. Ledebø and E. Meijer, Unpublished (see also E. Meijer, Thesis, Paper IV, Lund (1982)).
- 27 S. O. Hemila and R. H. Bube, *J. Appl. Phys.* 38, 5258 (1967).
- 28 J. S. Prener and D. J. Weil, *J. Electrochem. Soc.* 106, 409 (1959).
- 29 H. G. Grimmeiss, C. Ovrén and R. Mach, *J. Appl. Phys.* 50, 6328 (1979).
- 30 M. Godlewski, W. E. Lamb and B. C. Cavenett, *Solid State Commun.* 39, 595 (1981).
- 31 P. Besomi and B. W. Wessels, *J. Appl. Phys.* 53, 3076 (1982).
- 32 Y. Shirikawa and H. Kukimoto, *Solid State Comm.* 34, 359 (1980).
- 33 Y. Shirikawa and H. Kukimoto, *J. Appl. Phys.* 51, 5859 (1980).
- 34 K. Kosai, *J. Appl. Phys.* 53, 1018 (1982).
- 35 I. Broser, H. Mair and H. J. Schulz, *Phys. Rev.* 140, A2135 (1965).
- 36 C. S. Wang and B. M. Klein, *Phys. Rev. B* 24, 3393 (1981).
- 37 R. G. Humphreys, Private communication.
- 38 A. Ebina, E. Fukunaga and T. Takahashi, *Phys. Rev. B* 10, 2495 (1974).
- 39 L. G. Suslina, D. L. Federov, S. G. Konnikov, F. F. Kodzheshpirov, A. A. Andreev and E. G. Sharlai, *Sov. Phys. Semicond.* 11, 1132 (1977).
- 40 L. Soonckindt, D. Etienne, J. P. Marchand and L. Lassabatere, *Surf. Sci.* 86, 378 (1979).



